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A SERIES OF TEXTBOOKS FOR PERSONS ENGAGED IN ENGINEERING PROFESSIONS, TRADES, AND VOCATIONAL OCCUPATIONS
OR FOR THOSE WHO DESIRE INFORMATION CONCERNING THEM. FULLY ILLUSTRATED

INORGANIC CHEMISTRY FOR PHARMACY
STUDENTS
ELEMENTS OF VOLUMETRIC ANALYSIS
PHYSIOLOGY
PHARMACOLOGY AND TOXICOLOGY

SCRANTON
INTERNATIONAL TEXTBOOK COMPANY

1924

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PREFACE

The volumes of the International Library of Technology are made up of Instruction Papers, or Sections, comprising the various courses of instruction for students of the International Correspondence Schools. The original manuscripts are prepared by persons thoroughly qualified both technically and by experience to write with authority, and in many cases they are regularly employed elsewhere in practical work as experts. The manuscripts are then carefully edited to make them suitable for correspondence instruction. The Instruction Papers are written clearly and in the simplest language possible, so as to make them readily understood by all students. Necessary technical expressions are clearly explained when introduced.

The great majority of our students wish to prepare themselves for advancement in their vocations or to qualify for more congenial occupations. Usually they are employed and able to devote only a few hours a day to study. Therefore every effort must be made to give them practical and accurate information in clear and concise form and to make this information include all of the essentials but none of the non-essentials. To make the text clear, illustrations are used freely. These illustrations are especially made by our own Illustrating Department in order to adapt them fully to the requirements of the text.

In the table of contents that immediately follows are given the titles of the Sections included in this volume, and under each title are listed the main topics discussed. At the end of the volume will be found a complete index, so that any subject treated can be quickly found.

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INORGANIC CHEMISTRY FOR PHARMACY STUDENTS (PART 1)

FUNDAMENTAL LAWS AND DEFINITIONS

MATTER AND ITS SUBDIVISIONS

INTRODUCTION

1. The Beginning of Chemistry.—The history of chemistry, from its obscure beginning to the present time, when it has become indispensable to mankind, is an interesting one. To learn how chemistry developed to its present important position, one should know something about the various theories and about the different men closely connected with the development of the science.

The desire to change common metals like lead into the more precious gold gave rise to a class of men known as *alchemists*. To them is due the foundation of what has since developed into modern chemical science and industry, without which human progress would have been seriously retarded. It was not, however, until chemists began to study facts in relation to one another that certain fundamental laws were discovered and chemistry became a real science.

It was supposed in early times that earth, fire, water, and air were four elements that constituted everything in the universe, and it was not until the latter part of the eighteenth century that Priestly and Cavendish in England, Scheele in

Sweden, and Lavoisier in France proved that water is made up of the elements hydrogen and oxygen and that air consists chiefly of nitrogen and oxygen. These great discoveries have formed the groundwork for all chemical investigations down to the present time.

COMPOSITION AND DIVISION OF MATTER

2. Matter.—Each of the terms used in chemistry has a distinct and definite meaning that must be understood by any one who wishes to study the many laws and principles upon which the application of chemistry is based. Everything that one sees about him is subject to some kind of change that will alter its appearance, form, or chemical nature. Trees, grass, air, water, in fact, all kinds of things, have two points of similarity. They all occupy space and they have weight. The term **matter** is applied to anything that has weight and occupies space.

3. Properties of Matter.—A study of the different kinds of matter reveals the fact that each variety has peculiarities or characteristics by which it can be recognized and identified. For example, one can recognize a white substance as sugar, if it is white, sweet, and somewhat sticky. Qualities by which matter can be identified are called **properties of matter**. Whiteness, sweetness, and stickiness are properties of sugar. In general, color, taste, and feel are some of the properties of matter that enable one to distinguish different things from one another.

The separate particles of lump sugar differ from those of powdered sugar in size and shape, but they resemble each other in color, taste, and feel. One can change lump sugar to powdered by breaking up the former, thereby altering the size and shape of its particles. It is obvious, therefore, that some properties, such as size and shape, can be changed without destroying the nature of the substance, while others are constant and specific properties of a substance and cannot be changed without altering its chemical nature. To change the color and sweetness of sugar, one must change the sugar to something

else that is not sugar. Properties that can be changed without altering the chemical nature of the substance are called **conditional properties**, and properties that cannot be changed without altering the chemical nature of the substance are called **specific properties**.

From the foregoing, it is apparent that matter has characteristics that affect the senses in different ways. The color, size, and shape of matter have definite effects on sight; its odor on smell; its sweetness, sourness, and bitterness on taste; and its stickiness and smoothness on touch. These characteristics are called properties of matter.

4. Substances.—It is necessary to use the term *substance* properly, for it finds a wide application in chemistry. It can be considered as any form of matter that has distinct specific properties, no matter how much its conditional properties may vary. For example, sugar with its sweetness, whiteness, and slight stickiness, is a substance, for it retains these specific properties no matter how much its conditional properties, size and shape, may vary.

Steel is a substance, for it retains its specific properties, hardness, strength, luster, and color, no matter how much its conditional properties, shape and size, may be altered. It still remains the substance steel, even if made into a needle, rail, or axle.

Wood is a substance, for it retains its specific properties, its fibrous and fairly hard nature, no matter whether its form be that of a table, chair, or desk.

Matter, such as sugar, steel, or wood, retains its specific properties as long as its chemical composition remains the same. If one changes the chemical composition of sugar, the resultant product is no longer sugar, but something else with entirely different specific properties and with a different chemical composition. Hence, a **substance** is a form of matter that has a definite and constant composition.

5. Chemical and Physical Changes.—There is a distinction between changes that are *chemical* and changes that are *physical*. It is well to learn this distinction, for the whole

of the science of chemistry is based on changes of some sort. If sugar is broken into smaller pieces, it still remains sugar, for only the conditional properties, shape and size, have been altered. If, on the other hand, heat is applied to the sugar, it soon darkens, loses its whiteness and sweetness and becomes something other than sugar, for the specific properties, taste and color, of the substance sugar have disappeared. In other words, the chemical composition of the substance sugar has been altered. The first change, in which sugar retains its chemical composition, is called a *physical change*, while the second change, in which the substance sugar is changed to an entirely different substance by altering its chemical composition, is called a *chemical change*. Hence, changes that do not affect the composition of substances are called **physical changes**, and changes in which substances disappear and something else is formed in their place are called **chemical changes**.

As a further illustration: A lump of coal can be broken up and powdered finely without its color and hardness being destroyed; it still remains coal, even though changed in size and shape. This is a physical change. If, however, coal is burned, it loses its color and hardness, gives off a gas, and leaves a gray residue, called *ash*. The substance coal when burned loses its specific properties, by which it is identified, and forms new substances possessing other specific properties. This is a chemical change. It is apparent, therefore, that the specific properties of a substance are destroyed in a chemical change and are not affected in a physical change. In other words, a substance is not changed chemically as long as it retains its specific properties, and is changed chemically when its specific properties disappear.

6. Physics and Chemistry.—Like all other sciences, physics and chemistry treat of definite subjects. **Physics** is that branch of science that deals with changes that do not affect the composition of substances, and **chemistry** is that branch of science that treats of changes that affect the composition of substances. It should be borne in mind, however,

that chemical changes, as will be shown later, are always accompanied by physical ones, and it is almost impossible to study chemistry without keeping in mind the physical principles involved.

7. Organic and Inorganic Chemistry.—Chemistry is a broad science, for it treats of every change in the universe in which the composition of matter is involved. In a general way it may be stated that the two classes of substances recognized are those that contain the element *carbon* and those that do not contain it. The portion of chemistry that deals with substances containing carbon is called *organic chemistry*, and the portion that treats of substances other than those containing carbon is called *inorganic chemistry*. Some carbon compounds, such as carbon dioxide, carbon monoxide, carbonates, and carbon disulphide, are exceptions to these definitions, for they are described in both divisions of chemistry.

8. Mass.—It has been shown that everything in nature that has weight and occupies space is known as matter, but no reference has been made to the composition of the substances that make up the different kinds of matter, and as this subject is both interesting and important, it should be given careful thought.

Consider, as an example, common rock salt. A lump of this substance affects the senses in a definite way, for one can note its shape and size by sight; its saltiness by taste; its lack of odor by smell; and its sharp edges by touch. This lump of salt is a **mass** of matter; that is, a combination of matter appreciable to the senses.

9. Divisions of Matter.—The question naturally arises as to what constitutes a *mass* of matter, as to whether it is made up of particles, and, if so, as to how finely a mass can be divided by physical means without destroying its specific properties. Formerly, the view was held that all substances were continuous and there was no limit, theoretically, beyond which division could not be carried. This view has been discarded for the view, now accepted, that substances are composed of extremely small separate particles and that subdivision by physical means can be

repeated only until these minute particles are reached. Furthermore, these minute particles, called *molecules*, are conceived as having the same specific properties as the substances from which they are obtained. It should be borne in mind that *the molecule is merely a conception*, for it has never been actually isolated. A **molecule** then, may be defined as *the smallest particle of matter in which the original properties of the substance are retained*.

10. Hypothesis Defined.—The foregoing conception of molecules is known as the *molecular hypothesis* and is an excellent example of the line of reasoning often followed by scientists in their efforts to arrive at scientific truths. It is important, therefore, to understand the meaning of the term *hypothesis* at this point. Scientists note the various changes that take place, study them in detail, and seek to determine the causes for them. If no definite explanation results from their investigations, they proceed to imagine one; and then either prove or disprove it by tests. This imaginary explanation is called a **hypothesis**. The molecular hypothesis is today accepted as true, for tests all seem to verify and none seem to disprove it.

11. Molecules and Atoms.—Consider again the lump, or mass, of salt. Theoretically, but not actually, this mass can be subdivided repeatedly until an individual molecule of salt is obtained. If one were able to study this molecule of salt, he would note that it shows the same specific properties as the mass of salt; it has the same taste and no apparent odor. The molecule of salt differs from the mass only in conditional properties, such as size and shape; chemically, both the mass and molecule are the same, for the changes so far made are physical.

One naturally wonders whether the molecule can be divided further. From the foregoing discussion, it is obvious that the molecule cannot be divided by physical means, for a molecule is the smallest particle of a substance that can be obtained by physical means. There remain, however, chemical means by which division can be effected.

The *atomic hypothesis*, first advanced by Dalton, conceives the idea that molecules consist of *atoms*, particles that can be obtained, theoretically, by chemical means. Consider a molecule of salt. This substance has been found by experiment to contain two simple substances, *sodium* and *chlorine*, in chemical combination. Both the mass and molecule of salt have the chemical name *sodium chloride*. The elementary particles sodium and chlorine, of which a molecule of salt is made up, are called atoms and can be obtained from a molecule of sodium chloride only by chemical means. An **atom** is defined as the *smallest particle of matter that has yet been obtained by chemical means*; it is an undivided, though not an indivisible, unit of matter. The atom is taken as the unit of chemical changes. To illustrate the minute size of a molecule, it has been estimated that a molecule has a diameter of but a few ten-millionths of an inch.

12. Difference Between Chemical and Physical Changes.—The ultimate divisions of matter serve as the basis for simple definitions of chemical and physical changes. A physical change, as has been shown, can produce a molecule, but cannot affect its internal condition in any way, while a chemical change can act on a molecule to produce a change within it. Therefore, a **physical change** is one that does not affect a molecule and a **chemical change** is one that takes place within a molecule.

CHEMICAL AND PHYSICAL CHANGES

ELEMENTS AND THEIR COMBINATIONS

13. Elements and Compounds.—There are two kinds of molecules, those that contain similar atoms and those that contain dissimilar ones. Consider, for example, the substance *mercuric oxide*, each molecule of which contains one atom of *mercury* and one of *oxygen*. This substance, when heated, breaks up, or *decomposes*, into the two substances, mercury and oxygen. There are no unlike atoms in either of these latter

two substances, a molecule of oxygen containing nothing but oxygen atoms and a molecule of mercury nothing but a mercury atom; each is made up of but one kind of atom. So far, no one has been able to decompose either mercury or oxygen into simpler substances. Substances that have never been decomposed into simpler ones are called **elements**, and substances that can be decomposed into simpler substances are called **compounds**. Elements never contain unlike atoms and compounds always do.

So far as is now known, there are 83 substances that have not yet been decomposed into simpler substances. The majority of these are discussed in this Course. All kinds of matter consist of either these elements or combinations of them. Chlorine, each molecule of which contains two atoms of chlorine, is an example of an element. Sodium chloride, commonly called table salt, each molecule of which contains one atom of sodium and one of chlorine, is an example of a compound.

14. The Atomicities of Molecules.—The number of atoms in the molecules of the different elements is a subject that must be considered at this point for it has an important bearing on succeeding explanations. Depending upon whether the molecule of an element contains 1, 2, 3, 4, or 6 atoms, it is, respectively, known as *monatomic*, *diatomic*, *triatomic*, *tetramolecular*, or *hexatomic*. Molecules containing five atoms, or *pentatomic* molecules, are unknown. The atomicities of many of the elements have been determined experimentally, those of others have been found approximately; in a few cases the atomicity is uncertain.

The succeeding list shows the *probable* atomicity of many of the elements at ordinary temperatures, meaning anywhere between 0° C. and 100° C. In writing chemical equations, the usual atomicities of the elements will be employed throughout this Course. Referring to Table I, it should be noted that practically all the metals are monatomic.

15. Symbols and Formulas.—In indicating the composition of a substance, *symbols* are used instead of following the somewhat tedious practice of writing, in full, the names of

the different elements. The **symbols** are usually abbreviations consisting of the initial letters of the Latin names of the elements. As, however, there are over eighty elements and only twenty-six letters in the alphabet, nearly all of the symbols are composed of the initial letter and another distinctive letter selected from the name. Thus, the three elements carbon,

TABLE I
NAMES, ATOMICITIES, AND MOLECULAR FORMULAS OF
CHEMICAL ELEMENTS

Name and Atomicity of Element		Molecular Formula	Name and Atomicity of Element		Molecular Formula
Monatomic	Carbon.....	<i>C</i>	Diatomic	Iodine.....	<i>I₂</i>
	Lithium.....	<i>Li</i>		Bromine.....	<i>Br₂</i>
	Potassium.....	<i>K</i>		Chlorine.....	<i>Cl₂</i>
	Sodium.....	<i>Na</i>		Fluorine.....	<i>F₂</i>
	Barium.....	<i>Ba</i>		Oxygen.....	<i>O₂</i>
	Strontium.....	<i>Sr</i>		Hydrogen.....	<i>H₂</i>
	Calcium.....	<i>Ca</i>		Nitrogen.....	<i>N₂</i>
	Magnesium.....	<i>Mg</i>		Bismuth.....	<i>Bi₂</i>
	Mercury.....	<i>Hg</i>		Antimony.....	<i>Sb₂</i>
	Zinc.....	<i>Zn</i>		Sulphur.....	<i>S₂</i>
	Cadmium.....	<i>Cd</i>		Tellurium.....	<i>Te₂</i>
	Silver.....	<i>Ag</i>	Tetra- atomic	Ozone.....	<i>O</i>
	Gold.....	<i>Au</i>			
	Lead.....	<i>Pb</i>			
	Argon.....	<i>Ar</i>		Phosphorus.....	<i>P₄</i>
	Helium.....	<i>He</i>		Arsenic.....	<i>As₄</i>
	Krypton.....	<i>Kr</i>		Vanadium.....	<i>V₄</i>
	Neon.....	<i>Ne</i>			
	Xenon.....	<i>Xe</i>			
	Nickel.....	<i>Ni</i>			
	Copper.....	<i>Cu</i>			
	Aluminum.....	<i>Al</i>			

chlorine, and copper (cuprum) all have names commencing with the letter *C*; therefore, only carbon has received the letter *C* for its symbol, while *Cl* and *Cu* stand for chlorine and copper, respectively.

The application of these symbols for the purpose of showing the elements of a compound may be seen from an example, for

which purpose *sodium chloride*, commonly known as table salt, is selected. Instead of stating that one molecule of sodium chloride contains one atom of sodium and one atom of chlorine, the expression $NaCl$ is used. In this expression the symbol Na (Latin, *natrium*) stands for sodium and Cl for chlorine. A chemist can ascertain from this expression the exact composition of a molecule of sodium chloride. Similarly, saltpeter, known chemically as potassium nitrate, contains in each molecule one atom of potassium, one atom of nitrogen, and three atoms of oxygen. The combination may be indicated by the expression KNO_3 . The K stands for one atom of potassium (Latin, *kalium*), the N for one atom of nitrogen, and O_3 for three atoms of oxygen; such a combination of symbols showing the composition of a molecule is called a **formula**.

16. A number placed before a formula shows the number of molecules represented. For illustration, $2KCl$ represents 2 molecules of potassium chloride and $3KNO_3$ stands for 3 molecules of potassium nitrate.

A number placed to the right and a little below the symbol of an element shows the number of atoms of the element in 1 molecule. For example, H_2 means 1 molecule of hydrogen consisting of 2 atoms of hydrogen; $2K_2SO_4$ represents 2 molecules of potassium sulphate, *each molecule* of which contains 2 atoms of potassium, 1 atom of sulphur, and 4 atoms of oxygen. The 2 molecules of potassium sulphate contain, in all, 4 atoms of potassium, 2 atoms of sulphur, and 8 atoms of oxygen. Likewise, the formula $Ca(OH)_2$ represents 1 molecule of calcium hydroxide, which contains 1 atom of calcium, 2 atoms of oxygen, and 2 atoms of hydrogen, the subscript, 2, referring only to the contents of the parenthesis. The formula CaO_2H_2 for this substance, though also mathematically correct, is seldom used.

The foregoing principles are further illustrated by the following examples: NaI represents 1 molecule of sodium iodide containing 1 atom of sodium and 1 atom of iodine. H_2S represents 1 molecule of hydrogen sulphide containing 2 atoms of hydrogen and 1 atom of sulphur. $2KClO_3$ represents 2 mole-

cules of potassium chlorate, each molecule of which contains 1 atom of potassium, 1 atom of chlorine, and 3 atoms of oxygen; the two molecules contain, therefore, 2 atoms of potassium, 2 atoms of chlorine, and 6 atoms of oxygen. $2Ca(NO_3)_2$ represents 2 molecules of calcium nitrate, each molecule of which contains 1 atom of calcium, 2 atoms of nitrogen, and 6 atoms of oxygen; the two molecules contain 2 atoms of calcium, 4 atoms of nitrogen, and 12 atoms of oxygen.

17. Forms of Matter.—The divisions of matter so far considered are based on subdivision by physical and chemical means. There is also a classification based on the freedom with which molecules of matter can move about and with their own energy attract one another. The power to attract, or hold together, one another is called *cohesion* for like molecules and *adhesion* for unlike.

According to the theory of heat each and every molecule has a vibratory motion to and fro. In a *solid* the molecules are held closely together and kept from getting beyond a certain distance from one another by the attractive force between them. Still, they are at a considerable distance apart, compared with their diameters.

In *liquids* the distance through which a molecule may move is increased, and the force of adhesion that binds the molecules together is lessened.

In *gases* the molecular vibrations have increased to such an extent that the distance between any two molecules has become too great for the force of adhesion to become effective. The molecules are, therefore, following independent paths and are constantly colliding and rebounding in every direction.

18. Substances pass from one to another of these physical forms under changes of temperature and pressure. If, for example, a piece of ice, a solid, is heated sufficiently, it melts and forms water, a liquid. The molecules of ice, firmly held together by cohesion, can retain their original positions without being supported by some external, rigid body; that is, a square piece of ice will retain its shape without being supported by some vessel, such as a cup or a box. The molecules of water,

on the other hand, attract one another to a lesser degree than those of ice and are loosely held together; some external, rigid container, such as a cup, or a glass, is needed to hold the liquid in position. Water held in a certain shape by a container will not keep that shape when poured into a container of another shape but will assume the shape of the second container.

If water is heated further, it forms a gas, known as *steam*. The molecules of steam tend to follow independent paths and fly off into space, unless held in a closed containing vessel.

Based on the foregoing observations, the following definitions for the different physical forms of matter are deduced:

A *solid* is a form of matter in which the molecules cohere so rigidly that the object keeps its shape without support from surrounding bodies and is a form of matter that offers resistance to efforts to change its shape.

A *liquid* is a form of matter in which there is some cohesion among the molecules, but not enough to enable the material to keep its shape without support from a rigid containing vessel.

A *gas* is a form of matter in which molecules are too far apart to be able to attract one another and a gas is therefore a form of matter that tends to occupy the whole space in which it is confined.

The term *vapor* is sometimes used to refer to a substance, ordinarily a solid or a liquid, that has been changed to a gas.

19. Physical Condition of Chemical Elements.

Of all the elements, two, mercury and bromine, are ordinarily *liquids*; eleven of them, oxygen, hydrogen, chlorine, fluorine, nitrogen, argon, helium, krypton, neon, xenon, and niton, are *gases*; the rest of the elements are *solids*. Excepting carbon, the solid elements have been changed to liquids by means of heat; so far, carbon has been only slightly softened.

The changing of a solid to a liquid is called *fusing* or *melting*; the changing of a liquid to a solid is called *freezing* or *solidifying*; the changing of a gas to a liquid is called *liquefying*; the changing of a solid or a liquid to a gas is called *vaporizing*. As these terms are used constantly in chemistry, they should be thoroughly understood.

20. Mechanical Mixtures and Chemical Compounds.—It is necessary for students of chemistry and pharmacy to know when the addition of one substance to another results in a chemical or in a physical change. This distinction can be made clear by considering the mixing of sulphur, *S*, and iron, *Fe* (*ferrum*).

Sulphur is a pale-yellow substance that melts easily when heated, and dissolves in carbon disulphide, as will be explained further on. Iron is a dark-gray metallic substance that is readily attracted by a magnet and is not soluble in carbon disulphide.

When powdered sulphur and iron filings are rubbed together, the product, though differing in appearance from that of either of the constituents, is, in reality, the two original substances sulphur and iron, the various particles of which are arranged side by side and can be separated from each other by mechanical means. The iron can be removed by passing a magnet over the mixture and the sulphur can be freed from the iron by treating the mixture with carbon disulphide, a process that dissolves the sulphur and leaves the iron unaffected.

If heat is applied to this mixture of sulphur and iron, a noticeable change takes place, the final result being a black solid, resembling neither iron nor sulphur, for it is affected by neither a magnet nor carbon disulphide. It is an entirely new substance, known chemically as *ferrous sulphide*, *FeS*.

A mixture, such as that of sulphur and iron, previous to its being heated, is called a **mechanical mixture**, which is defined as a collection of substances, either elements or compounds, that retain their specific properties and can be separated by physical means. A substance, such as ferrous sulphide, is called a **chemical compound**, which is defined as a body produced by the chemical reaction between two or more substances and has specific properties different from the specific properties of any of the original substances.

CHEMICAL AFFINITY. ATOMIC AND MOLECULAR WEIGHTS

21. Attraction of Atoms.—On noting the many varied chemical changes in nature one is apt to wonder whether there is not some force or power that causes them. It is well, therefore, to consider this subject before proceeding further with the study of chemical laws and definitions.

Most atoms have a powerful, mutual attractive force, called **chemical affinity**, that binds atoms together to form molecules. This force is so strong that, while atoms can be made under certain conditions to exist alone for a short time, they always tend to rearrange themselves to form new molecules and cannot, therefore, continue to exist separately. Atoms, during the short time in which they exist alone, are said to be in the **nascent state**. When in this state, atoms possess greater chemical affinity than when combined with other atoms in a molecule. As a rule, the greater the difference in character between elements, the greater is the chemical affinity between their atoms. For example, chlorine and sodium, widely different in character, have a greater attraction for each other than sodium and potassium, elements that do not differ greatly in character.

22. Atomic Weights.—Chemists are able to calculate exactly the amounts, by weight, of different substances needed to produce chemical changes. As these calculations are based on the relative weights of atoms of elements, the following explanation of this subject should be carefully considered and studied.

As atoms cannot be altered, as far as we now know, each of them has a constant weight. Scientists have been able to determine, by experiment, the proportions by weight in which elements combine with one another. They found the element hydrogen to be the lightest of all atoms and, with this fact as a basis, determined how many times heavier the atoms of other elements are than that of hydrogen. For example, it was found by making experiments that hydrogen chloride, HCl , contains 1 part by weight of hydrogen to 35.19 parts by weight of chlo-

rine; that is, in 36.19 parts by weight of hydrogen chloride, there are 35.19 parts by weight of chlorine and 1 part by weight of hydrogen. Expressed in pounds, there are 35.19 pounds of chlorine and 1 pound of hydrogen in every 36.19 pounds of hydrogen chloride. Likewise, it has been found that there are 15.88 parts by weight of oxygen to every 2 parts of hydrogen in 17.88 parts by weight of water, H_2O . It should be borne in mind that these relative parts by weight are based on the fact that the weight of a hydrogen atom is taken as 1.

It is obvious from the foregoing that an atom of oxygen is 15.88 times as heavy as an atom of hydrogen and that an atom of chlorine is 35.19 times as heavy as an atom of hydrogen. The relative weights of atoms of other elements, compared with *hydrogen* as a standard, made equal to 1, have been determined by experiment. These relative weights are called **atomic weights**. For example, with hydrogen as a standard, the atomic weight of chlorine is 35.19, that of oxygen 15.88, and that of carbon 11.91.

23. Within recent years, the atomic weight system has been altered by making *oxygen*, instead of *hydrogen*, the standard of atomic weights. This system is represented by Table II. An examination of water, H_2O , under this system, shows that for every 16 parts by weight of oxygen there are present $2 \times 1.008 = 2.016$ parts by weight of hydrogen. The standard, oxygen, is assumed to have an atomic weight of 16 and all other weights are compared with it. As another illustration, calcium oxide, CaO , is found by experiment to contain, in every 56.07 parts by weight of it, 40.07 parts of calcium and 16 parts of oxygen; expressed otherwise, an atom of calcium has a relative weight of 40.07, when the atomic weight of oxygen is taken as 16. Values such as 1.008, for hydrogen, and 40.07, for calcium, are called the atomic weights of these elements, when oxygen is taken as the standard with a value of 16. Therefore, according to modern views, the **atomic weight** of an element is the relative weight of an atom of that element compared with the weight of an atom of oxygen which has a value of 16.

TABLE II
INTERNATIONAL ATOMIC WEIGHTS, 1921-22

Name	Symbol	Atomic Weight	Name	Symbol	Atomic Weight
Aluminum.....	<i>Al</i>	27.0	Molybdenum.....	<i>Mo</i>	96.0
Antimony (Stibium).....	<i>Sb</i>	120.2	Neodymium.....	<i>Nd</i>	144.3
Argon.....	<i>A</i>	39.9	Neon.....	<i>Ne</i>	20.2
Arsenic.....	<i>As</i>	74.96	Nickel.....	<i>Ni</i>	58.68
Barium.....	<i>Ba</i>	137.37	Niton (radium emanation).....	<i>Nt</i>	222.4
Bismuth.....	<i>Bi</i>	209.0	Nitrogen.....	<i>N</i>	14.008
Boron.....	<i>B</i>	10.9	Osmium.....	<i>Os</i>	190.9
Bromine.....	<i>Br</i>	79.92	Oxygen.....	<i>O</i>	16.00
Cadmium.....	<i>Cd</i>	112.40	Palladium.....	<i>Pd</i>	106.7
Cærium.....	<i>Cs</i>	132.81	Phosphorus.....	<i>P</i>	31.04
Calcium.....	<i>Ca</i>	40.07	Platinum.....	<i>Pt</i>	195.2
Carbon.....	<i>C</i>	12.005	Potassium (Kalium).....	<i>K</i>	39.10
Cerium.....	<i>Ce</i>	140.25	Praseodymium.....	<i>Pr</i>	140.9
Chlorine.....	<i>Cl</i>	35.46	Radium.....	<i>Ra</i>	226.0
Chromium.....	<i>Cr</i>	52.0	Rhodium.....	<i>Rh</i>	102.9
Cobalt.....	<i>Co</i>	58.97	Rubidium.....	<i>Rb</i>	85.45
Columbium.....	<i>Cb</i>	93.1	Ruthenium.....	<i>Ru</i>	101.7
Copper (Cuprum).....	<i>Cu</i>	63.57	Samarium.....	<i>Sa</i>	150.4
Dysprosium.....	<i>Dy</i>	162.5	Scandium.....	<i>Sc</i>	45.1
Erbium.....	<i>Er</i>	167.7	Selenium.....	<i>Se</i>	79.2
Europium.....	<i>Eu</i>	152.0	Silicon.....	<i>Si</i>	28.1
Fluorine.....	<i>F</i>	19.0	Silver (Argentum).....	<i>Ag</i>	107.88
Gadolinium.....	<i>Gd</i>	157.3	Sodium (Natrium).....	<i>Na</i>	23.00
Gallium.....	<i>Ga</i>	70.1	Strontium.....	<i>Sr</i>	87.63
Germanium.....	<i>Ge</i>	72.5	Sulphur.....	<i>S</i>	32.06
Glucinum (Beryl- lithium).....	<i>Gl</i>	9.1	Tantalum.....	<i>Ta</i>	181.5
Gold (Aurum).....	<i>Au</i>	197.2	Tellurium.....	<i>Te</i>	127.5
Helium.....	<i>He</i>	4.00	Terbium.....	<i>Tb</i>	159.2
Holmium.....	<i>Ho</i>	163.5	Thallium.....	<i>Tl</i>	204.0
Hydrogen.....	<i>H</i>	1.008	Thorium.....	<i>Th</i>	232.15
Indium.....	<i>In</i>	114.8	Thulium.....	<i>Tm</i>	169.9
Iodine.....	<i>I</i>	126.92	Tin (Stannum).....	<i>Sn</i>	118.7
Iridium.....	<i>Ir</i>	193.1	Titanium.....	<i>Ti</i>	48.1
Iron (Ferrum).....	<i>Fe</i>	55.84	Tungsten.....	<i>W</i>	184.0
Krypton.....	<i>Kr</i>	82.92	Uranium.....	<i>U</i>	238.2
Lanthanum.....	<i>La</i>	139.0	Vanadium.....	<i>V</i>	51.0
Lead (Plumbum).....	<i>Pb</i>	207.20	Xenon.....	<i>Xe</i>	130.2
Lithium.....	<i>Li</i>	6.94	Ytterbium (Neoytterbium).....	<i>Yb</i>	173.5
Lutecium.....	<i>Lu</i>	175.0	Yttrium.....	<i>Yt</i>	89.33
Magnesium.....	<i>Mg</i>	24.32	Zinc.....	<i>Zn</i>	65.37
Manganese.....	<i>Mn</i>	54.93	Zirconium.....	<i>Zr</i>	90.6
Mercury (Hydrargyrum).....	<i>Hg</i>	200.6			

24. Molecular Weights.—Knowing the number and the weights of the atoms in a molecule, one can easily find the weights of the molecules. In every case, the weight of a molecule is the sum of the weights of the atoms that it contains. The molecular weight of any compound is, then, equal to the sum of the atomic weights, as represented by the number of atoms in the molecule. As previously stated, a molecule of water, H_2O , contains 2.016 parts by weight of hydrogen and 16 parts of oxygen. Its molecular weight is the sum of the weights of all the atoms present in the molecule, in this case $2.016+16$, or 18.016.

One should learn to apply the atomic and molecular weights to calculations, for they are used in every phase of chemistry and are indispensable to the chemist in all kinds of industrial work. The application of Table II is shown by means of the following examples.

EXAMPLE 1.—Find the molecular weight of KCl , potassium chloride.

SOLUTION.—The formula shows that 1 molecule of potassium chloride contains 1 atom of each element. Hence, the weights given in Table II may be applied directly. Or,

Atomic weight of chlorine	=35.46
Atomic weight of potassium	=39.10

Molecular weight of potassium chloride=74.56. Ans.

EXAMPLE 2.—Find the molecular weight of Na_2O , sodium oxide.

SOLUTION.—According to the formula there are 2 atoms of sodium, Na . The weight given in Table II must therefore be multiplied by 2. Or,

$2 \times$ atomic weight of sodium	=46.00
Atomic weight of oxygen	=16.00

Molecular weight of Na_2O =62.00. Ans.

EXAMPLE 3.—Find the molecular weight of Na_2SO_4 , sodium sulphate.

SOLUTION.—The formula shows that there are 2 atoms of Na and 4 atoms of O ; hence, the atomic weights of these elements must be multiplied by 2 and 4, respectively. Or,

$2 \times$ atomic weight of sodium	= 46.00
Atomic weight of sulphur	= 32.06
$4 \times$ atomic weight of oxygen	= 64.00

Molecular weight of Na_2SO_4 =142.06. Ans.

EXAMPLE 4.—Find the molecular weight of $Ba(OH)_2$, barium hydroxide.

SOLUTION.—Referring to Art. **16**, it was stated that the subscript, 2, refers to the contents of the parenthesis; that is, *O* and *H*. There must, therefore, be 2 atoms of each. Or,

$$\text{Atomic weight of barium} = 137.370$$

$$2 \times \text{atomic weight of oxygen} = 32.000$$

$$2 \times \text{atomic weight of hydrogen} = 2.016$$

$$\text{Molecular weight of } Ba(OH)_2 = 171.386. \text{ Ans.}$$

EXAMPLE 5.—Find the molecular weight of $CaOCl_2$, chloride of lime.

SOLUTION.—In this example there is 1 atom of each element, except chlorine, of which there are 2. Hence,

$$\text{Atomic weight of calcium} = 40.07$$

$$\text{Atomic weight of oxygen} = 16.00$$

$$2 \times \text{atomic weight of chlorine} = 70.92$$

$$\text{Molecular weight of } CaOCl_2 = 126.99. \text{ Ans.}$$

NOTE.—The following Examples for Practice should be solved in the manner shown in the preceding examples, so as to acquire facility in calculations of this kind.

EXAMPLES FOR PRACTICE

Find the molecular weight of:

1. $CaCO_3$, calcium carbonate. Ans. 100.075
2. $PbCrO_4$, lead chromate. Ans. 323.20
3. $K_3Fe(CN)_6$, potassium ferricyanide. Ans. 329.218
4. $Mg(NH_4)_2(SO_4)_2$, magnesium ammonium sulphate. Ans. 252.52
5. $K_2Cr_2O_7$, potassium dichromate. Ans. 294.2

CHEMICAL EQUATIONS AND THEIR INTERPRETATION

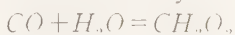
25. Chemical Equations.—It has been shown that elements and compounds are represented by symbols and formulas. The substances produced in chemical changes can be represented by them also. The substances *used* are placed before an equality sign and the products *formed* are placed after it; plus signs are placed between the substances on each side of the equation. Thus,



A chemist can tell from a glance at this chemical equation that when two molecules of sodium chloride are acted on by

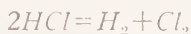
one molecule of hydrogen sulphate, known as sulphuric acid, one molecule of sodium sulphate and two molecules of hydrogen chloride, or hydrochloric acid, are formed.

There are some points regarding chemical equations that are important and worthy of special attention. First of all, *only changes that actually take place can properly be represented by chemical equations*. Many equations can be written so as to be mathematically correct; but, unless chemically true also, they are not acceptable as chemical equations. For example, the following equation is mathematically correct:



This equation is not a correct chemical equation because no one has, so far, been able to bring about the foregoing reaction. It should be borne in mind that *chemical equations are correct only when the changes they represent actually do take place*.

26. A careful study of chemical equations reveals certain facts by which the accuracy of them can be judged. Consider the equation representing the fact that two molecules of hydrochloric acid can be decomposed into one molecule of hydrogen and one of chlorine:



Each molecule of hydrochloric acid consists of 1 atom of hydrogen and 1 of chlorine; 2 molecules contain 2 atoms of hydrogen and 2 of chlorine. Likewise, 1 molecule of hydrogen contains, according to Table I, 2 atoms of hydrogen, and 1 molecule of chlorine contains 2 atoms of chlorine. There are, therefore, 4 atoms on each side of the equation. The same general principle holds true for all chemical equations and may be expressed in this way: The number of atoms on each side of the equation must be the same. There are 2 atoms of chlorine and 2 atoms of hydrogen on each side of the equation. Thus, *the number of atoms of any element on each side of a chemical equation must be the same*.

27. The quantities of various substances, as found by means of Table II, are important in chemical work, because they form the basis for most chemical calculations. The molecular weight of hydrochloric acid, as found by adding the

atomic weights of hydrogen and chlorine (Table II), is 36.468; $2HCl$ has a relative weight of 2×36.468 , or 72.936. Likewise, 1 molecule of chlorine and 1 molecule of hydrogen have the respective molecular weights 70.92 and 2.016; the sum is 72.936. It is apparent that the sum of the atomic weights on each side of this chemical equation is the same, as both are equal to 72.936. The following rule is based on this principle:

Rule.—*The sum of the atomic weights or molecular weights on each side of a chemical equation must be equal.*

A review of the foregoing facts shows that a chemical equation is correct only when it meets the following requirements:

1. It must represent a chemical change that takes place or that can be produced.
2. The sum of the atoms of any element on each side of the equation must be equal.
3. The sum of the atomic weights or molecular weights on each side of the equation must be equal.

28. Interpretation of Chemical Equations.—In addition to the foregoing facts that determine the correctness of a chemical equation, it is obvious that a chemical equation shows the relative number of atoms and molecules involved, and the relative weights of the substances needed and formed. For example, it has been found that 1 molecule of barium chloride, $BaCl_2$, reacts chemically with 1 molecule of sulphuric acid to form 1 molecule of barium sulphate, $BaSO_4$, and 2 molecules of hydrochloric acid; thus,



The sum of the relative weights on each side of the equation is the same:

The molecular weight of barium chloride is..	208.29
The molecular weight of sulphuric acid is...	98.076
Total	306.366
The molecular weight of barium sulphate is..	233.43
Twice the molecular weight of hydrochloric acid is	72.936
Total	306.366

The number of atoms of the various elements on each side of the equation is the same :

There are 2 atoms of chlorine, *Cl*; 1 of barium, *Ba*; 2 of hydrogen, *H*; 1 of sulphur, *S*; and 4 of oxygen, *O*, on each side of the equation.

The foregoing equation represents a chemical change that takes place, for it can be reproduced by adding sulphuric acid to a solution of barium chloride. The results show that the equation, as written, is correct. Furthermore, the equation shows that when 208.29 parts by weight of barium chloride combine with 98.076 parts by weight of sulphuric acid, they form 233.43 parts by weight of barium sulphate and 72.936 parts by weight of hydrochloric acid. The parts by weight may be expressed in terms of any unit of weight.

29. Use of Relative Weights.—The preceding explanations show that equations enable the chemist to determine a number of facts from the relative atomic weights. The application of relative weights in chemical equations is sufficiently important to be touched on, briefly, before proceeding to another subject.

The relative weights represented in a chemical equation, called **combining weights**, are used to calculate the weights of substances needed to produce a desired compound and are formed as a result of the combination. For example, calcium carbonate has been found, by experiment, to break up, when heated, into calcium oxide and carbon dioxide in this way :



Combining weights :

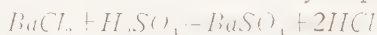
$$100.075 = 56.07 + 44.005$$

This equation is correctly written, for it represents a chemical change that actually takes place and it has the same number of atoms of each element and the same sum of combining weights on each side. Furthermore, the combining weights of the substances, calculated from Table II, show that every 100.075 parts by weight of calcium carbonate break up, when heated, into 56.07 parts by weight of calcium oxide and 44.005 parts by weight of carbon dioxide.

A chemist in his work may be asked to calculate the number of tons of calcium carbonate needed to produce 44.005 tons of carbon dioxide and the number of tons of calcium oxide, also produced. Relative weights form the basis for just such calculations as this one and are constantly applied in chemical work. It has already been shown that 100.075 parts by weight will produce 44.005 parts by weight of carbon dioxide and 56.07 parts by weight of calcium oxide. Hence, 100.075 tons of calcium carbonate are needed to produce 44.005 tons of carbon dioxide, while 56.07 tons of calcium oxide are left. In like manner, being given the weight of either calcium carbonate or calcium oxide, one can calculate the weights of the other substances formed or needed.

CONSERVATION AND TRANSFORMATION OF MATTER

30. Indestructibility of Matter.—A study of chemical changes shows that the sum of the weights of the substances used is equal to the sum of the weights of the products formed. Consider again, for example, the change that takes place when barium chloride is acted on by sulphuric acid. Or,



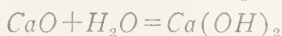
From the atomic weights of the elements present, it is apparent, as previously shown, that 208.29 parts by weight of barium chloride and 98.076 parts by weight of sulphuric acid produce 233.43 parts by weight of barium sulphate and 72.936 parts by weight of hydrochloric acid; that is, 306.366 parts by weight of the substances used form 306.366 parts by weight of products. In other words, the sum of the weights of materials used is equal to the sum of the weights of the products formed.

The fact that neither more nor less by weight of products is formed than is used, is true of all chemical changes and leads to an important chemical law, which may be expressed in this way: *Whenever a change takes place in the composition of substances, the weight of the matter after the change is the same as the weight before the change.*

31. Conservation of Energy.—Closely allied to the law regarding the indestructibility of matter is the law relating to

the conservation of energy. Heat, light, electricity, and the like, all have capacities for doing work; each of these agencies can bring about physical and chemical changes. These influences are forms of **energy**, which term is defined as *the capacity of a body for doing work*. Unlike matter, energy neither has weight nor occupies space.

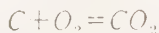
In all chemical changes, energy is either given off or absorbed. If, for instance, calcium oxide, commonly called *quicklime*, is mixed with water, considerable energy in the form of heat is given off and *slaked lime* is produced. Thus,



Similarly, energy in the form of heat must be added to change calcium carbonate into calcium oxide and carbon dioxide.

The various forms of energy can be converted into one another. Suppose, for example, that the heat under a boiler in an electric plant is used to generate steam, which in turn causes an engine to produce motion; the motion can be used to run a dynamo and produce electricity; if the current of electricity is passed through an incandescent lamp, light and heat are evolved. It is seen that the form of energy, heat, passes to other forms, such as motion, electricity, and light. If it were possible to produce these transformations in some form of apparatus from which no form of energy could escape, the amount of energy at the beginning of the transformation would be found to be the same as that at the finish. The fact that neither a creation nor a destruction of energy has ever been observed has resulted in the law regarding the conservation of energy, expressed as follows: *Energy cannot be created or destroyed*.

32. Chemical Energy.—One naturally wonders where the coal gets its heat, since energy cannot be created. The coal burns, that is, combines with oxygen to form carbon dioxide; thus,



A considerable amount of energy in the form of light and heat is liberated during this change. It is, therefore, apparent

that there was some kind of energy stored up in the coal and that it was liberated when the coal reacted with oxygen to form carbon dioxide. Like all other forms of energy, that one contained in the coal, called **chemical energy**, has a capacity for doing work. Chemical energy is stored up in many substances other than coal. Thus, the heat liberated when calcium oxide is mixed with water is chemical energy contained in the former.

It is apparent from the foregoing that chemical changes are always accompanied with some kind of an energy transformation; chemical energy may be changed to some other form, or another form may be converted to chemical energy.

33. Exothermic and Endothermic Reactions.

When substances react to form new compounds, heat is either given off or it is absorbed. This absorption or evolution of heat may not be apparent, but, nevertheless, may be measured by the use of suitable apparatus.

Those reactions in which heat is given off are described as being **exothermic**. Examples are the formation of *NaOH* when sodium and water react, or when hydrogen and chlorine react to form hydrochloric acid. An **endothermic** reaction is just the reverse of the above; that is, in this type, heat is absorbed. Examples are: The formation of carbon bisulphide from carbon and sulphur (described later) or the formation of chlorine and hydrogen, when hydrochloric acid is decomposed.

LAW OF DEFINITE PROPORTIONS

34. Valence.—The different formulas of substances, so far mentioned, show that 1 atom of an element attracts different numbers of atoms of other elements. For instance, 1 atom of barium combines with 2 of chlorine, as in barium chloride, *BaCl₂*; 1 of sodium with 1 of chlorine, as in sodium chloride, *NaCl*; 1 of carbon with 2 of oxygen, as in carbon dioxide, *CO₂*; 1 of calcium with 1 of oxygen, as in calcium oxide, *CaO*. The capacity of combinations is called **valence** and is defined as *the combining capacity possessed by an atom of an element*. By means of the valence, one can tell how many atoms of one element can unite with an atom of another element.

Valence should not be confused with chemical affinity for each has its own distinctive chemical significance. *Valence* refers to the *number* of atoms of one element that can unite with an atom of another element, while *chemical affinity* treats of the relative *power of attraction* possessed by elements. An illustration will probably make this distinction clear. Consider the elements chlorine, barium, and sodium. Chlorine and sodium have been found, by experiment, to have a greater chemical affinity for each other than have chlorine and barium, yet 1 atom of barium can unite with twice as many chlorine atoms as 1 atom of sodium, because barium has a valence twice that of sodium. If all three elements are present, chlorine and sodium will unite much more readily than will chlorine and barium, because the chemical affinity between chlorine and sodium is greater than that between chlorine and barium. It is obvious, therefore, that chemical affinity and valence have entirely different meanings.

35. The valence of each element, as determined by actual experiments, affords chemists a valuable source of information, when writing chemical equations and formulas; special efforts should, therefore, be made to remember the different valences of each element as given in Table III. It has been determined that no element has a valence lower than that of hydrogen, which is taken as unity, or 1. The valence of every other element is expressed in terms of this unit. Some elements have different valences, depending on the element with which it combines. For example, nitrogen has five valences. Chlorine, 1 atom of which combines with 1 atom of hydrogen, has a valence of 1; it is therefore said to be *monovalent* or *univalent*, and is called a *monad*. Oxygen, 1 atom of which combines with 2 of hydrogen, always has a valence of 2; it is said to be *divalent* and is called a *dyad*. Nitrogen has a variable valence, but when it combines with 3 atoms of hydrogen, it has a valence of 3; it is then said to be *trivalent*, and is called a *triad*. Carbon, 1 atom of which combines with 4 atoms of hydrogen, has a valence of 4; it is said to be *tetravalent*, and is called a *tetrad*. Likewise, atoms combining with 5 or 6 atoms of a monovalent atom, such as hydrogen, are said to be *pentavalent* or *hexa-*

TABLE III
USUAL VALENCE OF ELEMENTS

Name of Element	Symbol	Valence	Name of Element	Symbol	Valence
Aluminum.....	<i>Al</i>	3	Nickel.....	<i>Ni</i>	2, 3
Antimony (Stib- ium).....	<i>Sb</i>	3, 5	Nitrogen.....	<i>N</i>	1, 2, 3, 4, 5
Arsenic.....	<i>As</i>	3, 5	Osmium.....	<i>Os</i>	2 to 8
Barium.....	<i>Ba</i>	2	Oxygen.....	<i>O</i>	2
Bismuth.....	<i>Bi</i>	3, 5	Palladium.....	<i>Pd</i>	2, 4
Boron.....	<i>B</i>	3	Phosphorus.....	<i>P</i>	3, 5
Bromine.....	<i>Br</i>	1, 3, 5, 7	Platinum.....	<i>Pt</i>	2, 4
Cadmium.....	<i>Cd</i>	2	Potassium		
Cæsium.....	<i>Cs</i>	1	(Kalium).....	<i>K</i>	1
Calcium.....	<i>Ca</i>	2	Praseodymium..	<i>Pr</i>	3
Carbon.....	<i>C</i>	4	Rhodium.....	<i>Rh</i>	2, 3, 4
Cerium.....	<i>Ce</i>	3, 4	Rubidium.....	<i>Rb</i>	1
Chlorine.....	<i>Cl</i>	1, 3, 5, 7	Ruthenium.....	<i>Ru</i>	2 to 8
Chromium.....	<i>Cr</i>	2, 3, 6	Samarium.....	<i>Sm</i>	3
Cobalt.....	<i>Co</i>	2, 3	Scandium.....	<i>Sc</i>	3
Copper (Cuprum).	<i>Cu</i>	1, 2	Selenium.....	<i>Se</i>	2, 4, 6
Erbium.....	<i>Er</i>	3	Silicon.....	<i>Si</i>	4
Fluorine.....	<i>F</i>	1	Silver (Argentum)	<i>Ag</i>	1
Gallium.....	<i>Ga</i>	3	Sodium		
Germanium.....	<i>Ge</i>	2, 4	(Natrium).....	<i>Na</i>	1
Glucinum (Beryl- ium).....	<i>Gl</i>	2	Strontium.....	<i>Sr</i>	2
Gold (Aurum)....	<i>Au</i>	1, 3	Sulphur.....	<i>S</i>	2, 4, 6
Hydrogen.....	<i>H</i>	1	Tantalum.....	<i>Ta</i>	5
Indium.....	<i>In</i>	3	Tellurium.....	<i>Te</i>	2, 4, 6
Iodine.....	<i>I</i>	1, 3, 5, 7	Terbium.....	<i>Tb</i>	3
Iridium.....	<i>Ir</i>	3, 4	Thallium.....	<i>Tl</i>	1, 3
Iron (Ferrum)....	<i>Fe</i>	2, 3, 6	Thorium.....	<i>Th</i>	4
Lanthanum.....	<i>La</i>	3	Tin (Stannum) ..	<i>Sn</i>	2, 4
Lead (Plumbum) .	<i>Pb</i>	2, 4	Titanium.....	<i>Ti</i>	3, 4
Lithium.....	<i>Li</i>	1	Tungsten.....	<i>W</i>	2 to 6
Magnesium.....	<i>Mg</i>	2	Uranium.....	<i>U</i>	4, 6
Manganese.....	<i>Mn</i>	2, 3, 4, 6, 7	Vanadium.....	<i>V</i>	2 to 5
Mercury			Ytterbium		
(Hydrargyrum) .	<i>Hg</i>	1, 2	(Neoytterbium) .	<i>Yb</i>	3
Molybdenum.....	<i>Mo</i>	2, 3, 4, 6	Yttrium.....	<i>Yt</i>	3
Neodymium.....	<i>Nd</i>	3	Zinc.....	<i>Zn</i>	2
			Zirconium.....	<i>Zr</i>	4

valent, and are called *pentads* or *hexads*, respectively. In each compound that will be considered in inorganic chemistry, the valence of each element in the compound will be satisfied. For instance, take the compound ferric oxide, Fe_2O_3 . Since oxygen always has a valence of 2, three oxygen atoms have 6 valences to be satisfied by two iron atoms; therefore, Fe , or iron, has a valence of 3. If two divalent elements, barium, Ba , and oxygen combine to form a compound such as barium oxide, the formula is not Ba_2O_2 , but the simpler form, BaO , and as each element has a valence of 2, the valence of each is satisfied.

36. Law of Definite Proportions.—The different subjects so far considered in connection with chemical combinations all tend to prove the fact that chemical reactions are based on definite principles to which there are no exceptions. The subjects of atomic weights, valence, and the number of atoms reacting all lead to the general principle that there is a definite and fixed way in which different quantities of elements combine to form new substances.

Consider, for example, the compound magnesium oxide, MgO , resulting from the union of magnesium, Mg , and oxygen, O . The atomic weight of magnesium is, according to Table II, 24.32 and that of oxygen is 16. The molecular weight of magnesium oxide is equal to the sum of the atomic weights of magnesium and oxygen, or $24.32 + 16.0 = 40.32$. These figures show that every 40.32 parts by weight of magnesium oxide contain 24.32 parts by weight of magnesium and 16 parts by weight of oxygen. Investigations of magnesium oxide, no matter in what way the substance may have been made, show that these relative weights are always the same; that there is never any ratio between magnesium and oxygen other than 24.32 : 16.—A ratio between two terms, such as x and y , is generally expressed as $x : y$, in which x and y are the values being compared; it is read: x to y . The ratio may also be written as a fraction, $\frac{x}{y}$.

Magnesium and oxygen being divalent, 1 atom of each is contained in magnesium oxide. The ratio of the number of

magnesium atoms to the number of oxygen atoms has never been found to be other than 1 : 1; neither have any elements other than magnesium and oxygen ever been found in magnesium oxide.

The foregoing observations can be summed up in a general way by stating that each molecule of magnesium oxide always consists of 1 atom of magnesium and 1 of oxygen in the same proportion by weight. They verify *the law of definite proportions*, which states that *a chemical compound always contains the same constituents in the same proportion by weight*. This law forms a basis for every application of valence and of atomic weights. The principles of valence and of atomic weights are correctly used only when they are in accord with the aforementioned broad principle covered by the law of definite proportions.

37. Law of Multiple Proportions.—Some elements, as shown in Table III, have more than one valence and can combine with some other element to form more than one compound. Consider, for example, tin and chlorine. The former has valences of 2 and 4 and the latter a valence of 1 when combined with metals like tin. These elements form stannous chloride, SnCl_2 , and stannic chloride, SnCl_4 . By means of the atomic weights given in Table II, one is able to calculate the parts by weight of chlorine that unite with a fixed weight of tin. For instance, the atomic weight of tin is 118.7 and that of chlorine is 35.46. There are, in stannous chloride, SnCl_2 , $35.46 \times 2 = 70.92$ parts by weight of chlorine to every 118.7 parts by weight of tin; likewise, there are, in stannic chloride, SnCl_4 , $35.46 \times 4 = 141.84$ parts by weight of chlorine to every 118.7 parts by weight of tin. The parts by weight of chlorine combined in stannous chloride and stannic chloride, combined with 118.7 parts by weight of tin, bear a ratio to each other of 70.92 : 141.84. Reducing the terms of this ratio to their lowest values by dividing by 70.92, the ratio becomes 1 : 2. This ratio is called a simple one, because it can be expressed in whole numbers.

The foregoing illustration is an example of *the law of multiple proportions*, which may be stated as follows: *When two*

elements combine to form more than one compound, the weights of the one that unite with a fixed weight of the other bear a simple ratio to each other.

38. Avogadro's Law.—Investigation of the uniform behavior of gases under changes of temperature and pressure has resulted in the *law of Avogadro*, which states that *equal volumes of all gases, under the same condition of temperature and pressure, contain the same number of molecules*. For example, suppose that a certain volume of hydrogen gas contains 10,000 molecules of hydrogen (H_2); an equal volume of any other gas, as for example, oxygen (O_2) will, under the same conditions of temperature and pressure, also contain 10,000 molecules of oxygen. Since 10,000 molecules of oxygen occupy a volume equal to that occupied by 10,000 molecules of hydrogen, under the same conditions of temperature and pressure, 1 molecule of each gas will occupy the same volume, or amount of space. Hence, a molecule of one gas will occupy a volume equal to that of a molecule of any other gas, under the same conditions of temperature and pressure. This hypothesis applies only to gases, not to liquids and solids.

39. Avogadro's Law Applied to Chemical Equations.—It has already been shown that 2 molecules of hydrochloric-acid gas can be decomposed into 1 molecule of chlorine gas and 1 molecule of hydrogen gas, the equation representing this change being $2HCl = H_2 + Cl_2$.

As 1 molecule of hydrochloric-acid gas occupies a volume equal to that occupied by either 1 molecule of hydrogen or 1 of chlorine, the chemical change may be expressed in terms of gaseous volumes, as follows:

As 2 volumes of hydrochloric-acid gas decompose to form 1 volume of hydrogen and 1 of chlorine, it follows that 2 liters of hydrochloric acid must give 1 liter of hydrogen and 1 liter of chlorine.

The application of Avogadro's law will be shown by the following examples:

EXAMPLE 1.—If 2 molecules of ammonia gas can be decomposed into 1 molecule of nitrogen gas and 3 molecules of hydrogen gas, how many

liters of nitrogen and of hydrogen can be obtained from 2 liters of ammonia?

The equation to be applied is: $2NH_3=N_2+3H_2$.

SOLUTION.—As ammonia, nitrogen, and hydrogen are all gases, the equation may be read: 2 volumes of ammonia decompose to form 1 volume of nitrogen and 3 volumes of hydrogen. If 2 liters of ammonia are used, each volume of ammonia may be considered as 1 liter. Hence, the equation shows that 2 liters of ammonia decompose to form 1 liter of nitrogen and 3 liters of hydrogen. Ans.

EXAMPLE 2.—One molecule of hydrogen can combine with 1 of chlorine to form 2 molecules of hydrochloric-acid gas. What volumes of hydrogen and chlorine are needed to form 10 liters of hydrochloric-acid gas?

The equation to be applied is: $H_2+Cl_2=2HCl$.

SOLUTION.—As all of the substances shown in the equation are gases, it may be read: 1 volume of hydrogen unites with 1 volume of chlorine to form 2 volumes of hydrochloric-acid gas. Since 10 liters of hydrochloric-acid gas are required, the volume of each gas is equal to $10 \div 2 = 5$ liters. The equation, therefore, shows that 5 liters of hydrogen and 5 liters of chlorine are needed to form 10 liters of hydrochloric-acid gas. Ans.

EXAMPLE 3.—One atom of carbon combines with 1 molecule of oxygen to form 1 molecule of carbon-dioxide gas. How many cubic centimeters of carbon dioxide are formed by the action of 100 cubic centimeters of oxygen on carbon?

The equation to be applied is: $C+O_2=CO_2$.

SOLUTION.—Applying the law of Avogadro, the equation shows that for every volume of oxygen used there is formed 1 volume of carbon-dioxide gas. As this law applies only to gases, the volume relation cannot be applied to carbon, which is a solid. Since 100 cubic centimeters of oxygen are used, each volume of gas may be considered as equal to 100 cubic centimeters. Hence, 100 cubic centimeters of oxygen react with carbon, volume unknown, to form 100 cubic centimeters of carbon-dioxide gas. Ans.

PHYSICAL PROCESSES

APPARATUS AND METHODS

INTRODUCTION

40. Principal Types of Apparatus.—The best work can be done by a pharmacist, when he is thoroughly familiar with the names and uses of the various kinds of apparatus needed to perform experiments and to make tests. The different types of apparatus shown on Plates I, II, and III will be described in detail in connection with the many operations dealt with in different parts of the text. It is advisable, however, to learn to associate the appearance of each piece of apparatus illustrated, with its name, for it is knowledge that will be helpful in practical laboratory work. For this purpose each illustration is provided with the name of the instrument, apparatus, tool, etc., that it is intended to represent.

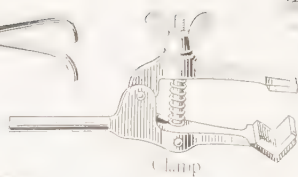
METHODS OF SEPARATION

41. Classification of Methods.—There are some operations in laboratory work that are constantly applied, particularly in the separation of substances from one another. These methods are of such general use that it is well for the pharmacist to know what details must be observed and what points must be noted in them. In each case, advantage is taken of the fact that a constituent to be separated from a mixture has some property not possessed by the rest of the constituents.

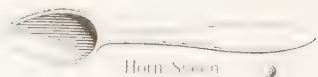
The principal methods of separation are: *Solution, decantation, filtration, crystallization, evaporation, distillation, sublimation, and ignition*. The details to be observed in each of these processes should be studied carefully, for they find con-



Long



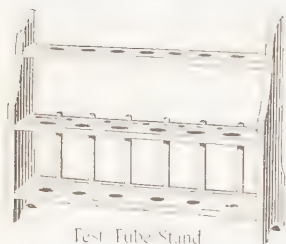
Clamp



Horn Spoon



Water Bath



Test Tube Stand



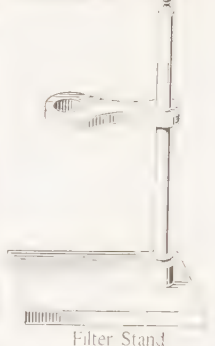
Separatory Funnel



Pipette



Hydrometer



Filter Stand



Spatula



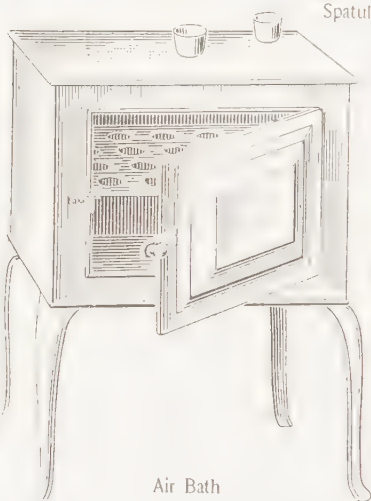
Forceps



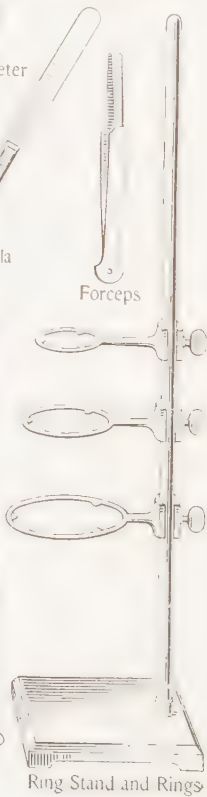
Tripod



Fish-Tail Burner

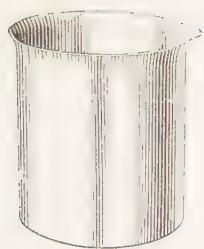


Air Bath



Ring Stand and Rings

PLATE I



Beaker



Volumetric Flask



Crucible and
Cover



Boiling Flask



Wash Bottle



Distilling Flask



Woulf's Bottle



Watch Glass



Graduated Flask



Filter Flask



Wash Bottle



Blowpipe



Cylinders



Sand Bath

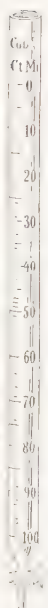


Evaporating Dish

PLATE II



U Tube



Burette



Funnel



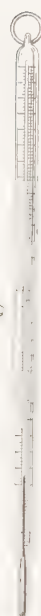
Bain Marie



Triangle



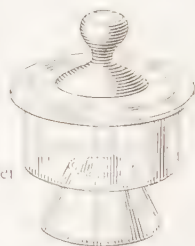
Tubing Clamp



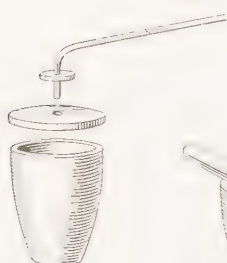
Thermometer



Test Tubes



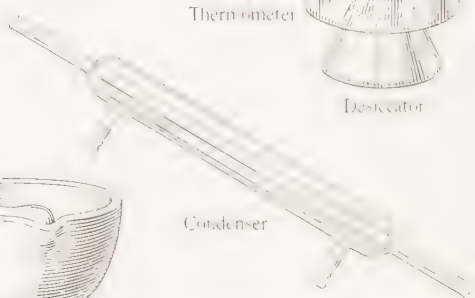
Desiccator



Rose Crucible



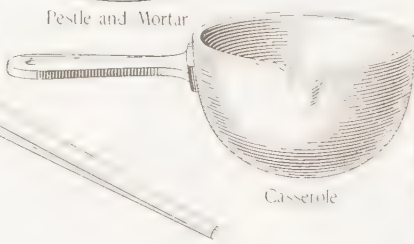
Pestle and Mortar



Condenser



Retort



Casseroles



Alcohol Lamp

PLATE III

stant application in chemical work and are indispensable in laboratory operations. Only the details of operation are treated of in this part of the text, the principles upon which they are based being explained in another Section.

42. Solution, Decantation, and Evaporation.—If common table salt is placed in water, it soon disappears and leaves a clear liquid mixture. The salt is said to have **dissolved** in the **solvent**, water, to form a **solution** of salt in water. The theory of solutions is important and extensive enough to be considered at length in another Section. Increasing the surface area of a substance by powdering it and heating the solvent, after adding the substance to it, enables one to hasten the solution. A mortar and pestle are generally used to powder substances.

The fact that a substance is *soluble* enables it under certain circumstances to be separated from other substances. Suppose, for example, that a mixture of sand and salt is to be separated into its constituents. It has been determined that sand is **insoluble** (cannot be dissolved) in water and that salt is **soluble** (can be dissolved); facts that enable one to separate the substances completely.

The mixture is shaken up with water, a process that dissolves the salt and leaves the sand unaffected. The sand is allowed to settle to the bottom and the clear solution on top, called the **supernatant liquid**, is carefully poured off into a basin without disturbing the settled sand. The operation of pouring off a supernatant liquid without disturbing the sediment is called **decantation**. **Washing by decantation** is accomplished by pouring off the supernatant liquid, adding fresh water, mixing thoroughly, allowing the insoluble substance to settle, and again pouring off the supernatant liquid.

If heat is applied to the vessel containing the salt solution, water passes off as steam and crystals of salt form in the basin. The conversion of a liquid to a vapor is called **evaporation**, a process that is used extensively in chemical operations.

Either a test tube or a beaker can be used as the vessel in which salt, water, and sand are mixed; an evaporating dish

serves as the vessel in which to collect the salt solution and from which to evaporate the water. Heat can be applied by means of either a Bunsen burner or an alcohol lamp; a piece of wire gauze is generally placed on a tripod, and the basin containing the salt solution is placed on the gauze.

43. Filtration.—Unlike the sand mentioned in the foregoing article, there are some solids so finely divided that they float in a liquid and settle only with difficulty, in which case the process of decantation cannot be used. **Filtration**, the operation that must be used in this instance to separate the soluble substance from the insoluble, is the process of separating a liquid from an insoluble substance by pouring the mixture onto a porous material, in which case the liquid passes



FIG. 1

through the pores and the insoluble substance remains on the porous material.

For illustration, suppose that a mixture consisting of powdered chalk and salt is to be separated into its constituents. The mixture is thoroughly shaken with water to dissolve the salt and is then poured onto a folded filter paper, arranged in a glass funnel. The solution of salt will pass through the paper and the chalk will remain on the paper. The liquid that passes through the porous material during filtration is called the **filtrate**. Asbestos, talc, and cotton are porous materials often used for filtering purposes. In every case, one should wet a filter paper after it has been placed in a funnel and before any of the material to be filtered is introduced.

44. Fig. 1 shows how a filter paper is folded for use in a funnel. A piece of soft porous paper, as shown at 1 (blotting

paper 3 inches in diameter will do for ordinary practice), is doubled twice and then opened into a cone, taking three folds of the paper on the one side and one on the other, as shown at 2 and 3, respectively. The cone of paper is placed in a glass funnel and moistened with water. Care should be taken that the point of the folded filter is not broken.

As filtration is one of the most important of all processes used in the laboratory, one should observe carefully every detail upon which the operation depends. As an illustration, let it be supposed that a solution of sodium carbonate is added to a solution of barium chloride.

A white insoluble substance is formed, as a result of a chemical combination that will be described in another Section. This insoluble substance is called a **precipitate**, which is defined as an insoluble substance formed from a solution.

Precipitation, the process of forming a precipitate, is brought about, as a general rule, by the formation of an insoluble substance, as a result of a chemical action between two soluble substances in solution.



Let it be supposed that the precipitate, formed when the solution of sodium carbonate is added to the solution of barium chloride, is to be separated from the rest of the mixture. The solution and precipitate are poured onto the filter by holding a glass rod or thin piece of glass tubing against the lip of the beaker or test tube, and by tipping the vessel containing the mixture, as shown in Fig. 2. The clear liquid, or filtrate, passes through the pores of the paper and is collected in a suitable vessel, such as a beaker;

the precipitate remains on the paper. Some clean water is poured on the paper and the precipitate is washed free from any soluble substances that have not yet passed through the paper.

Care should be taken, when pouring the mixture onto the filter, to hold the glass rod or thin glass tubing close to the filter paper in order to guard against spattering or the liquid running down on the outside of the vessel. A wash bottle is generally used, as shown in Fig. 3, to supply the water needed to wash the soluble substances through the paper. The wash



FIG. 3

bottle is also used, as shown in Fig. 4, to remove the last portion of the mixture from the vessel containing it.

45. Crystallization.—A mixture may contain two soluble substances that differ from each other in their degree of solubility. In cases such as this, the mixture is completely dissolved by boiling. As the solution cools, the less soluble substances will separate out in a definite shape and the more soluble substances will remain in solution. The process in which a soluble substance separates from a solution, as a definitely shaped body, is called **crystallization**, and the definitely shaped body is called a **crystal**.

For example, a mixture of equal parts of potassium chlorate and potassium chloride is placed in a test tube and just enough

water is added to dissolve the substances upon boiling. On allowing the solution to cool, crystals of the less soluble potassium chlorate will separate from the solution. These crystals may be removed from the solution by filtration, then purified by washing with a small amount of cold water, and then dried at a very low temperature.

46. Fractional Crystallization.—If equal parts of sodium and potassium nitrates are dissolved in about 25 per cent. excess of hot water, that is, 25 per cent. more water than is actually necessary for the solution of the above salts, and the solution then slowly cooled, potassium nitrate will crystallize first and then the sodium nitrate. Each lot of crystals may be



FIG. 4

redissolved and the process of cooling and crystallization repeated, each repetition of the process resulting in the further purification of the two salts.

47. Distillation.—In the case of a mixture of a liquid and a solid or a mixture of two or more liquids, it is sometimes necessary to separate the component parts of the mixture into the original constituents; in this case the process of *distillation* is used. **Distillation** is a process, in which a substance is first liquefied, if it is a solid, by means of heat, or if already a liquid, it is evaporated, or volatilized, by the application of heat to the containing vessel, the volatile matter, or vapor, then being passed through a **condenser** and again liquefied or **condensed**.

For example, if it is desired to separate a mixture containing colored matter and water (a water-ink mixture will answer), the work may be done as follows: The mixture is placed in the round-bottomed distillation flask *a*, Fig. 5, which is connected to the condenser *b* and which also contains the thermometer *d*. Heat is applied to the flask by means of the modified Bunsen burner *h*, the flask being supported by means of an iron ring, covered with a piece of wire gauze and clamped to the ring

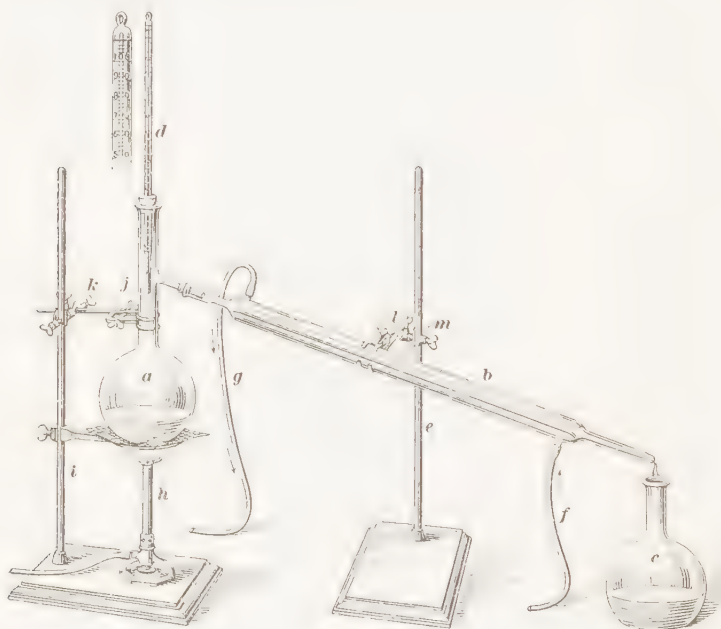


Fig. 5

stand *i*. The flask is held in its vertical position by means of the universal clamp *j* and the clamp holder *k*. When the liquid in the flask begins to boil or distil, the vapors pass through the side tube of the flask into the condenser, which is supported by the ring stand *e*, the universal clamp *l*, and the clamp holder *m*. This condenser is kept cold by the water entering at *f* and leaving at *g*. When the vapors strike the cold inner tube of the condenser, they liquefy or condense and are collected in the flat-bottomed Florence flask *c*, which in this case

acts as the **receiver**. The condensed liquid, termed the **condensate** or **distillate**, is the water of the original mixture. It will be found to be perfectly clear, the coloring matter of the ink being left behind as a **residue** in the distilling flask.

48. Fractional Distillation.—This operation may be illustrated as follows: Suppose there is a solution of benzene and xylene, two organic coal-tar products, and that it is required to separate them as completely as possible by means of distillation. The boiling point of benzene is 80° C. while that of xylene is about 142° C. Taking 100 cubic centimeters of a mixture, containing 50 cubic centimeters of each, and distilling it, the greater part of the benzene will come over first while, as the distillation proceeds, the distillate will become richer and richer in xylene. Then, if in the first distillation two portions, or fractions, of 50 cubic centimeters each, had been collected, the first would have contained most of the benzene and the second most of the xylene. Now, if these fractions are again separately distilled and other fractions collected at 10° C. below and above the boiling points of benzene, in the one case, and of xylene, in the other, it will be seen that if this procedure is continued for a sufficient number of distillations, two fractions will ultimately be obtained, which will consist of nearly pure benzene and xylene. Of course, results as good as these can hardly be obtained with the ordinary laboratory apparatus, but they may be obtained by employing specially designed distilling apparatus.

49. Sublimation.—Most solids, as, for example, ice, will first form a liquid and then a vapor, when heated. There are a few solids, however, such as iodine, ammonium chloride, camphor, etc., which pass directly from a solid form to that of a vapor, when heated, without first forming liquids. The distillation of substances that condense directly into solids, without forming liquids, is called **sublimation** and the condensed substances are called **sublimates**.

The process of sublimation is sometimes used to separate substances from one another. For example, if a mixture of sand and ammonium chloride is placed in a test tube and then

heated, dense white fumes of ammonium chloride are given off which, upon cooling, condense in the upper part of the tube as a white sublimate. The sand in the mixture is unaffected.

Substances that can be distilled, evaporated, or sublimed are called **volatile** and those that cannot be are called **non-volatile** bodies.

50. Ignition.—Some substances burn and form gases and others do not. This fact affords another means of separating substances that form a mixture. The substance that burns and generally forms a gas, called a **combustible** substance, passes from the mixture and leaves the substance that does not burn, called an **incombustible** substance, behind. The process of heating a substance intensely is called **ignition**.

As an example, suppose that charcoal and sand are to be separated from each other. If this mixture is heated to redness, the pure charcoal (carbon), a combustible substance, burns and forms a gas, carbon dioxide; the sand, an incombustible substance, remains behind.

51. Catalysis.—The term **catalysis** is given to a form of action by which a substance appears to exert a chemical effect without itself changing. Thus, hydrogen peroxide may be decomposed into water and oxygen by means of gold or silver, neither of which are altered in the least in the process of decomposition, but each exerts a catalytic action.

52. Effervescence, Deliquescence, Efflorescence. *Effervescence* is the escape of a gas from a liquid in which it is either generated or has been held by pressure, as carbonic acid gas obtained from dissolving marble, or from soda water. *Deliquescence* is the dissolving of a substance in water, which it absorbs from the moisture present in the air. Examples are sodium and potassium hydroxides. Such substances are said to be *hygroscopic*, although all hygroscopic substances do not dissolve in the absorbed water. *Efflorescence* is the gradual crumbling of a crystal to powder on exposure to the air, due to the escape of the water necessary for the formation of the crystal. Examples are: Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

METHODS AND UNITS OF MEASUREMENT

METRIC WEIGHTS AND MEASURES

53. Fundamental Units.—The *metric system* is commonly used by chemists and pharmacists for expressing quantities by weight and measure.

In the **metric system** the fundamental unit of length is the *meter*, equal to 39.37 inches, and from it are derived the units of capacity and weight, called, respectively, the *liter* and the *gramme*. All other units of the metric system are decimal sub-

TABLE IV
PREFIXES OF THE METRIC SYSTEM UNITS

Prefixes and Unit	Meaning of Prefixes	Names of Units
milli-.....	one-thousandth = $\frac{1}{1000} = .001$	$\left\{ \begin{array}{l} \text{meter (for length)} \\ \text{gramme (for weight)} \\ \text{liter (for capacity)} \end{array} \right.$
centi-.....	one-hundredth = $\frac{1}{100} = .01$	
deci-.....	one-tenth = $\frac{1}{10} = .1$	
unit-.....	one, or 1	
deka-.....	ten, or 10	
hecta-.....	one hundred, or 100	
kilo-.....	one thousand, or 1000	

divisions and multiples of these fundamental units; that is, they are tenths, hundredths, etc., and ten times, one hundred times, etc., the meter, liter, and gramme.

The meter, liter, and gramme bear a simple relation to one another for *1,000 cubic centimeters are equal in capacity to that of 1 liter, and 1 liter of pure water at 4° C. weighs 1,000 grammes.*

54. Abbreviations of Units.—The following abbreviations are used to represent the various units:

M. =meter	kg. =kilogramme
dm. =decimeter	Gm. =gramme
cm. =centimeter	dg. =decigramme
mm. =millimeter	mg. =milligramme
L. =liter	dl. =deciliter
ml.=milliliter or mil (formerly cubic centimeter or Cc.)	

TABLE V
MEASURES OF LENGTH, SURFACE, VOLUME, CAPACITY, AND WEIGHT

MEASURES OF LENGTH

10 millimeters (mm.)	=1 centimeter (cm.)
10 centimeters	=1 decimeter (dm.)
10 decimeters	=1 meter (M.)
10 meters	=1 dekameter (dkm.)
10 dekameters	=1 hectometer (hm.)
10 hectometers	=1 kilometer (km.)

MEASURES OF SURFACE

100 square millimeters (sq. mm. or mm ² .)	=1 square centimeter (sq. cm. or cm ² .)
100 square centimeters	=1 square decimeter (sq. dm. or dm ² .)
100 square decimeters	=1 square meter (sq. m. or m ² .)

MEASURES OF VOLUME

1,000 cubic millimeters (cmm. or mm ³ .)	=1 cubic centimeter (ccm., c. c., or cm ³ .)
1,000 cubic centimeters	=1 cubic decimeter (cdm. or dm ³ .)
1,000 cubic decimeters	=1 cubic meter (m ³ .)

MEASURES OF CAPACITY

10 milliliters (ml.)	=1 centiliter (cl.)
10 centiliters	=1 deciliter (dl.)
10 deciliters	=1 liter (L.)
10 liters	=1 dekaliter (dkl.)
10 dekaliters	=1 hectoliter (hl.)
10 hectoliters	=1 kiloliter (kl.)

MEASURES OF WEIGHT

10 milligrammes (mg.)	=1 centigramme (cg.)
10 centigrammes	=1 decigramme (dg.)
10 decigrammes	=1 gramme (Gm.)
10 grammes	=1 dekagramme (dkg.)
10 dekagrammes	=1 hectogramme (hg.)
10 hectogrammes	=1 kilogramme (kg.)
1,000 kilogrammes	=1 ton (t.)

55. Metric Units Commonly Used by Chemists and Pharmacists.—The following table includes practically all of the weights and measures of the metric system that are commonly used by the chemist and the pharmacist.

TABLE VI

FUNDAMENTAL UNITS EMPLOYED BY CHEMISTS

1,000 cubic centimeters (c. c.) = 1,000 mils = 1 liter (L.)
 1,000 grammes (Gm.) = 1 kilogramme (kg.)
 1,000 millimeters (mm.) = 1 meter (M.)

56. Metric and English Units Conversion Factors.

The following factors are often used to convert measures and weights of one system into terms of another:

Pounds avoirdupois $\times .4536$ = kilogrammes.

Ounces avoirdupois $\times 28.35$ = grammes.

Kilogrammes $\times 2.2046$ = pounds avoirdupois.

Grammes $\times .035274$ = ounces avoirdupois.

Pounds Troy $\times .3732$ = kilogrammes.

Kilogrammes $\times 2.6792$ = pounds Troy.

Ounces Troy $\times 31.103$ = grammes.

Grammes $\times .032151$ = ounces Troy.

Grammes $\times 15.432$ = grains.

Grains $\times .0648$ = grammes.

Pounds per cubic inch $\times 27.7$ = grammes per cubic centimeter.

Pounds per cubic foot $\times 16.02$ = kilogrammes per cubic meter.

Grammes per cubic centimeter $\times .0361$ = pounds per cubic inch.

Milligrammes per liter = parts per million.

Grains per U. S. gallon $\times 17.138$ = parts per million.

Parts per million $\times .583$ = grains per U. S. gallon.

Gallons $\times 3.7854$ = liters.

Liters $\times .26417$ = gallons.

Liters $\times 1.0567$ = liquid quarts.

Liquid quarts $\times .94636$ = liters.

Liters $\times .9081$ = dry quarts.

Dry quarts $\times 1.101$ = liters.

Fluid ounces $\times 29.57$ = cubic centimeters.

Cubic centimeters $\times .0338$ = fluid ounces.

Meters $\times 1.09361$ = yards.

Yards $\times .914402$ = meters.

Centimeters $\times .3937$ = inches.

Inches $\times 2.54001$ = centimeters.

Miles $\times 1.60935$ = kilometers.

Cubic feet $\times 28.32$ = liters.

METHOD OF WEIGHING

57. The Analytical Balance.—As a knowledge of the correct manipulation of an analytical balance is of importance to the pharmacist, as well as to the chemist, a general description of the balance and its operation will be given at this point.

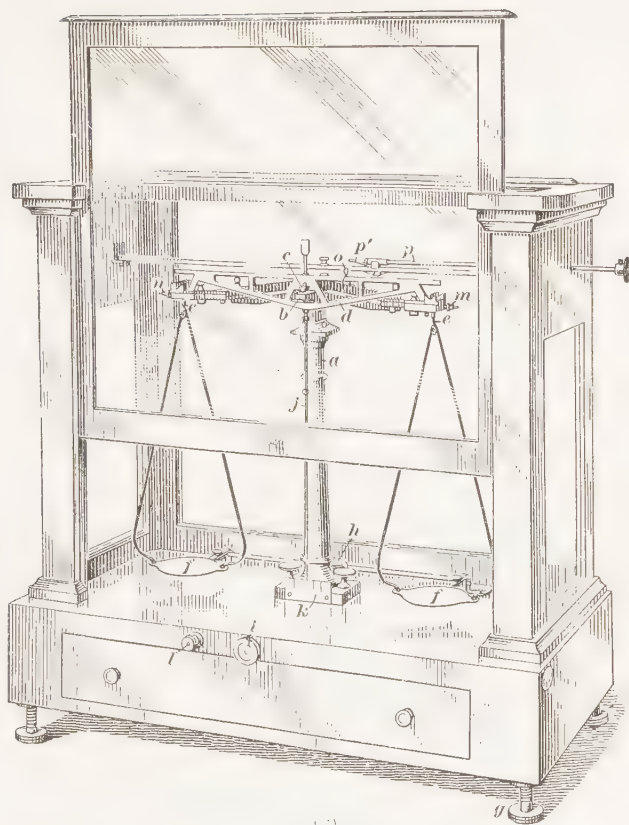
The balance illustrated in Fig. 6 (*a*) has a capacity of 200 grammes and is sensitive to a weight of one-twentieth of a milligramme. The balance is enclosed in a glass case fitted with sliding doors in front and in back. The drawer in the base contains the weights, brushes, spatula, etc. At the top of the hollow pillar *a* is embedded a rectangular-shaped piece *b* of agate, on which rest the agate knife edges *c* of the beam *d*. The stirrups *e*, from which the scale pans *f* are suspended, also rest on agate knife edges. At *g* are shown the leveling screws by which the case may be adjusted so as to bring the air bubble in the spirit level *h* into a central position.

The knob *i* operates a rod, placed in the pillar *a*, by means of which the beam may be lifted slightly off its bearings, or knife edges. This is the position to be occupied by the beam when the balance is not in use. By turning the knob *i* in the required direction, in this case to the left, the beam is lowered upon its knife edges and the balance is ready for weighing operations.

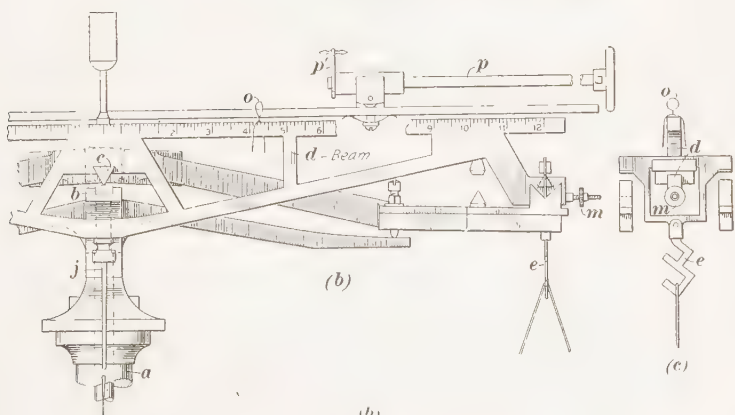
58. As the materials to be weighed have a more or less corrosive action on metals, the pans *f* carry balanced watch glasses on which the chemicals are placed. However, if non-corrosive solids are to be weighed, the pan at the left is provided with an aluminum scoop-shaped pan the weight of which is exactly balanced by a special weight placed on the other pan. It is important to ascertain if the two pans are in perfect balance, in which case the pointer, or index, *j* should come to rest at the zero mark of the scale *k*, when the beam is released.

How far this is the case may be tested in the following manner: The balance is released by turning the knob *i* to the left; also, the scale pans are released by pushing in the knob *l* and turning it to the right. The beam and the pans are now

A. E. D. 1894



(a)



(b)

(c)

(b)

FIG. 6

free to swing and if the pointer moves over the same number of scale divisions on either side of the zero mark, it indicates that the pans are in balance.

Should the pointer swing farther to the left of the zero mark, it proves that the right-hand pan is too heavy and that balance must be established by means of the screws *m* and *n*. In this case the screw *m* would be turned so as to bring it nearer the pillar *a*; or, the screw *n* would be turned in the same direction, thus bringing it farther away from *a*. Either of the screws should be given only a few turns at a time, testing the results and repeating the operations until the pointer swings over the same number of divisions on either side of the zero mark, coming finally to rest at this point.

Fig. 6 (*b*) is an enlarged view of the right-hand end of the beam, partly broken away. In this view the rider *o* is clearly shown; also, the arm *p'* on the rod *p* by which the rider is moved into position. At the end of the beam is seen the adjusting screw *m*. At (*c*) is an end view of the beam, corresponding parts in all the views being indicated by similar letters.

59. The operation of weighing consists in placing the substance to be weighed on the left-hand watch glass and the required number of weights on the other glass to produce a balance between the two pans and thus compelling the pointer to come to rest at the zero mark. The smallest separate weight that may be used for the right-hand pan weighs 10 milligrams. In order to weigh closer than this, it is necessary to employ the platinum rider *o*, shown resting on the beam *d*, Fig. 6. This rider weighs 10 milligrams, and is known as a *10-milligram rider*. When placed on the beam at the division marked *10*, it produces the same effect as a 10-milligram weight placed on the right-hand pan. If this rider is moved to the division *1* of the beam or at any other division up to *12*, the effect produced corresponds with that obtained from placing a corresponding number of milligrams on the right-hand pan. In some balances there is a rider for each end of the beam and either one may be placed into position by means of the rods *p*.

60. The weights are usually kept in a box, as shown in Fig. 7. The larger weights are generally made of brass and sometimes gold-plated; the smaller ones are made of aluminum or platinum. Each small weight rests in a separate compartment under a glass lid *a b*. For the purpose of lifting the weights, a forceps is used, which has its place in the box.

Accurate weights must under no consideration be touched with the fingers, but always lifted with the forceps.

The arrangement of the weights varies with different makes. Fig. 7 shows the usual and most convenient arrangement for a set of weights of from 100 grammes to .0001 gramme.

Before attempting to weigh, the student must learn not only the denomination of each weight, but also its place in the box.



FIG. 7

He must be quite as well able to read the weights he has placed in the balance pan from the empty space in the box as from the weights themselves.

SPECIFIC GRAVITY AND DENSITY

61. Definitions and Examples.—As the terms *specific gravity* and *density* are constantly used in chemistry, their meaning should be well understood. This subject is fully dealt with in *Pharmacy*, Part 1; it will, therefore, be only briefly referred to at this place.

The specific gravity of any solid or liquid is equal to the ratio between its weight and the weight of a like volume of water.

For example, zinc is found to be 7.15 times as heavy as an equal volume of pure water at 4° C., the temperature at which water has its greatest density. The value 7.15 is, therefore, the specific gravity of zinc. The term density is often used instead of specific gravity in connection with liquids and solids.

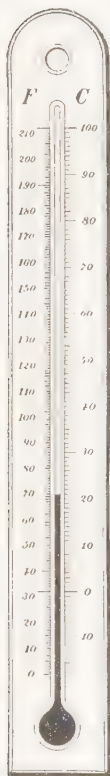


FIG. 8

62. *The specific gravity of any gas is equal to the ratio between its weight and the weight of an equal volume of air.*

The density of a gas is equal to the ratio of its weight to the weight of an equal volume of hydrogen.

For example, it is found that oxygen is 1.4292 as heavy as an equal volume of air. Its specific gravity is, therefore, 1.4292. On the other hand, it is found that oxygen is 15.87 times as heavy as an equal volume of hydrogen. Hence, its density is 15.87.

MEASUREMENT OF TEMPERATURE

63. Thermometers.—Chemists and pharmacists must use instruments to measure the intensity of heat, that is, temperature, for heat has a strong influence on chemical action. Based on the fact that heat causes substances to expand, an instrument, called a **thermometer**, is constructed to measure the temperature. The substance used in it, usually mercury, is sensitive to heat changes and affords a means of determining the temperature.

The mercury in the tube of the thermometer, Fig. 8, expands and rises as the temperature increases and contracts and falls as the temperature decreases. While thermometers differ in construction and materials, they are all based on the same principle.

64. Temperature Scales.—Thermometers are marked off into divisions, as shown in Fig. 8, each of which is called a **degree** and is expressed as 1° . The ordinary house thermometer, generally used in the United States, is based on the Fahrenheit scale. In this scale, the freezing point of pure water is called 32° F. and the boiling point 212° F. The space between the 32° F. and the 212° F. is divided into 180 equal parts, each one of which is called a degree Fahrenheit, expressed as 1° F. The scale is usually extended below and above 32° F. and 212° F., respectively, using the same divisions.

In the centigrade scale, generally used by chemists, the freezing point of water is called 0° C. and the boiling point 100° C. The divisions representing degrees are secured by dividing the space between 0° C. and 100° C. into 100 equal parts; these divisions are also extended below 0° C. and above 100° C.

65. It is frequently necessary to change from one scale to the other, in which case the following two rules are observed:

Rule I.—*To change from Fahrenheit to centigrade, subtract 32 from the temperature, Fahrenheit, multiply the result by 5, and divide by 9.*

Rule II.—*To change from centigrade to Fahrenheit, multiply the temperature, centigrade, by 9; divide the result by 5, and add 32.*

EXAMPLE 1.—Convert 41° F. to its corresponding centigrade temperature.

SOLUTION.—Applying rule I, $41-32=9$; $9 \times 5=45$; $45 \div 9=5$. Hence, 41° F. corresponds to 5° C. Ans.

EXAMPLE 2.—Convert 10° C. to its corresponding Fahrenheit temperature.

SOLUTION.—Applying rule II, $10 \times 9=90$; $90 \div 5=18$; $18+32=50$. Hence, 10° C. corresponds to 50° F. Ans.

EXAMPLE 3.—Convert -14° C. into Fahrenheit temperature.

SOLUTION.—Applying rule II, $-14 \times 9=-126$; $-126 \div 5=-25.2$; $-25.2+32=6.8^{\circ}$ F. Ans.

EXAMPLE 4.—Convert -13° F. into centigrade temperature.

SOLUTION.—Applying rule I, $-13-32=-45$; $-45 \times 5=-225$; $-225 \div 9=-25^{\circ}$ C. Ans.

PRACTICAL HINTS

PHYSICAL OPERATIONS

66. Heating Glass.—Glass is one of the most useful of all materials to the chemist or pharmacist in his work, for it is transparent, can be put into different shapes, when hot and plastic, and is unaffected by most chemicals. It is, however, brittle, a property that makes it liable to break, unless it is handled with care.

Heat should never be applied to glass unevenly, lest the glass expand unevenly and thereby crack. A wire gauze is used when heating liquids in glass vessels to keep the flame from

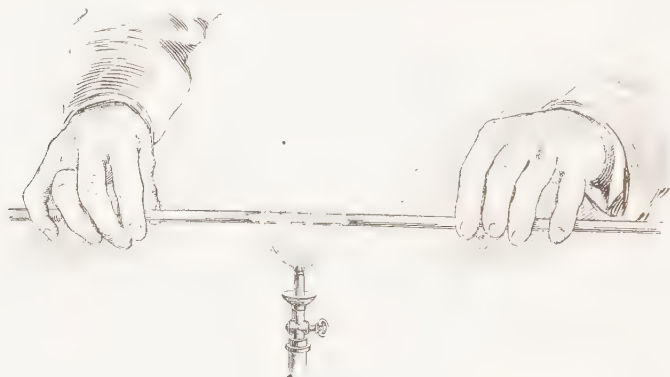


FIG. 9

coming into direct contact with the glass and to secure an even distribution of heat. In this way, equal expansion of all parts of the glass is obtained and there is little danger of the glass vessels cracking.

67. Bending and Drawing Glass Tubing.—Heat will make glass so soft that it can be bent into various shapes. Hold one end of the glass tube, to be bent, in each hand and place it lengthwise in a flat flame (generally produced by a fish-tail burner), as shown in Fig. 9; do not use the direct flame of the Bunsen burner for this work, for it will cause the glass to

crease at the bend. Keep turning the glass slowly in the flame at the point where you wish to bend it until it softens and

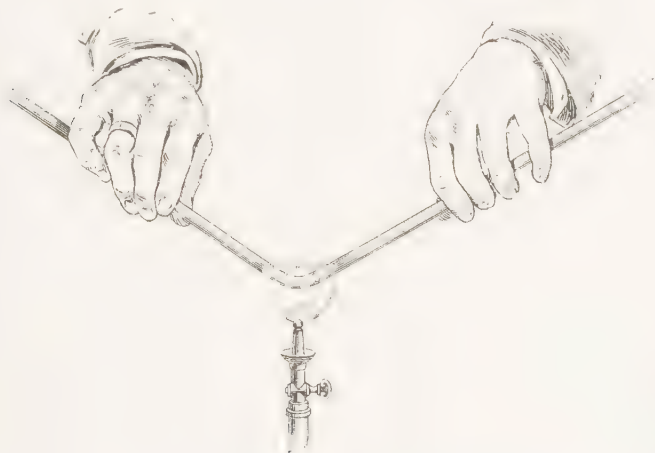


FIG. 10

begins to sag. Then raise the ends, as shown in Fig. 10, until the desired bend is obtained. Care should be taken to soften the glass thoroughly before bending it; precautions should also be taken to keep turning the tube in the flame lest heat be applied to only one side, resulting in the bend being flat instead of even and round.

To make a *capillary* tube, as at *BA*, Fig. 11, the tube should be heated, as in the foregoing operation, at some middle point and when the glass becomes soft, it should be removed from the flame and the ends of the tube quickly pulled in opposite directions. The result will be the tube illustrated in Fig. 11. The section *BA* is a thin-walled *capillary* tube, short lengths of which are used for melting point determinations. (See *Organic Chemistry for Pharmacy Students*.) If the tube is cut at a point between



FIG. 11

BA, each part may be connected to the gas supply and used as a jet. In this manner, a very small pencil-pointed flame may be obtained which is used in a variety of ways in chemistry.

68. Cutting Glass Tubing.—A pharmacist often needs to cut a piece of glass tubing to a desired length, a task that is easily accomplished. Make a nick in the glass tube with a sharp-edged file and then hold the tube in both hands; the two forefingers should be together immediately under the nick and the two thumbs above. Turn the wrists outwards and downwards, as though trying to widen the nick in the tubing, until the tube breaks. Fig. 12 illustrates this operation.

69. Rounding the Ends of Glass Tubing.—A pharmacist often needs to round the sharp end of a piece of glass



FIG. 12

tubing so that he can slide it through rubber or cork stoppers without difficulty and can insert it into rubber tubing without cutting the inside walls of the latter. The rounding is best accomplished by holding the sharp end in a Bunsen-burner flame until it begins to soften, at which time it becomes smooth and round. A moistened end will pass into a stopper or rubber tube more readily than a dry one. For this reason, a little vaseline is sometimes rubbed around a tube end or it is dipped into water before inserting it.

NOMENCLATURE

NAMES OF CHEMICAL COMPOUNDS

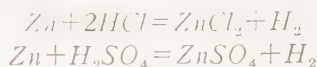
ACIDS, BASES, AND SALTS

70. General Remarks.—In olden times, names were applied to substances without following any fixed plan. Today, however, when the chemical composition of nearly every substance is known, substances referred to in chemistry are named according to a plan in which the chemical composition of the substance plays the most important part. No one can consider his education in chemistry satisfactory, until he thoroughly understands the system followed in naming substances and knows how to apply it. One should know the proper use of names like *acid*, *base*, *salt*, *peroxide*, *sulphide*, *chlorate*, *chlorite*, and many other terms. The following explanation of this subject should be considered carefully, for it treats of the definitions and rules upon which the naming of substances is based and is applicable to *every branch of chemistry*.

71. Acids.—It is well to consider some of the substances called *acids* to determine whether there are any specific characteristics that distinguish them from all other substances. Sulphuric acid and hydrochloric acid are two substances used a great deal by chemists and pharmacists. Their formulas, H_2SO_4 and HCl , respectively, show that they both contain hydrogen, but so do many other substances that are *not* acids, as, for example, calcium hydroxide, $Ca(OH)_2$, potassium hydroxide, KOH , and water, H_2O . How does the hydrogen in acids, therefore, differ from the hydrogen in other substances?

Acids, when mixed with metals, as, for example, zinc and iron, chemically combine with them and liberate hydrogen.

Following is the reaction that takes place when zinc reacts with each acid mentioned:



In the first case, zinc chloride and hydrogen are formed; in the second, zinc sulphate and hydrogen are produced. It has been found by experiment that acids are the only substances of those containing hydrogen that can react with metals or equivalent elements to form the products hydrogen and salts. Therefore, acids contain hydrogen that can be replaced by metals.

It has also been found that acids can change the color of *litmus*, a vegetable dye of indefinite chemical composition, from *blue* to *red*. Other substances do not act on litmus to produce this effect.

From the foregoing facts, it is obvious that acids have distinct characteristics possessed by no other class of substances, and that the following definition will apply: *An acid is any substance containing hydrogen, which readily replaces its hydrogen by metals, with the liberation of hydrogen, and that changes the color of blue litmus to red.*

72. Bases.—Hydroxides that change the color of red litmus to blue and feel soapy to the touch, when dissolved in water are commonly called **bases**. The oxides that possess the same properties are sometimes called bases also. Bases react chemically in a way that is directly opposite to that of acids; in fact, a chemical reaction between a base and an acid results in a product possessing the properties of neither acids nor bases. If the color of red litmus is changed to blue it indicates an *alkaline reaction* and if the color of the blue litmus is changed to red it indicates an *acid reaction*. The hydroxides of calcium, $\text{Ca}(\text{OH})_2$, barium, $\text{Ba}(\text{OH})_2$, strontium, $\text{Sr}(\text{OH})_2$, sodium, NaOH , ammonium, NH_4OH , and potassium, KOH , are common examples of bases.

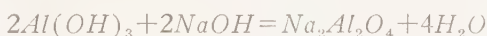
73. Metals and Non-Metals.—Elements that form basic hydroxides and can replace hydrogen in acids are called **metals**. They all have what is known as a metallic luster,

when in compact form. In powdered form, however, most of them appear black. For example, magnesium, a metal that is lustrous in compact form, is gray when powdered.

Non-metals neither have a metallic luster nor replace hydrogen in acids. Their oxides and hydroxides generally give acid reactions. In combination with hydrogen or hydrogen and oxygen, they all form acids.

The dividing line between metals and non-metals is, however, not a sharp one, for some elements can act either as metals or non-metals, depending on the conditions. For example, silicon appears as a metal in silicon disulphide, SiS_2 , and as a non-metal in metasilicic acid, H_2SiO_3 . Elements that commonly act both as metals and non-metals are called **metalloids**. Metals are called *positive elements* and non-metals *negative elements*, based on their action during *electrolysis*, a subject that will be treated in another Section.

Table VII shows the divisions into which the important elements are conveniently grouped. It should be borne in mind, however, that the classification is somewhat arbitrary, for some elements classed as metals will, under certain conditions, act as non-metals. For example, aluminum ordinarily acts as a metal; yet, when its compounds chemically react with sodium hydroxide, they form sodium aluminate, in which substance aluminum acts as a non-metal, thus:



74. Salts.—The term **salt** is ordinarily applied to sodium chloride. In chemistry, however, it refers to the products formed when the hydrogen atoms of acids have been replaced by metals. The majority of substances included in inorganic chemistry come under this heading. To illustrate the formation of a salt: Zinc reacts with sulphuric acid to form hydrogen and the salt zinc sulphate; thus,



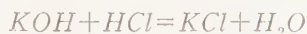
The metal portion of a salt, in this case zinc, is called the *positive radical*, and the acid portion with which the metal is combined, in this case SO_4 , is called the *negative radical*. The negative radical of an acid is always the portion of the acid that

TABLE VII
METALS AND NON-METALS

Metals		Non-Metals
Names	Names	Names
Aluminum	Neodymium	Argon
Antimony	Nickel	Arsenic
Barium	Osmium	Boron
Bismuth	Palladium	Bromine
Cadmium	Platinum	Carbon
Cæsium	Potassium	Chlorine
Calcium	Praseodymium	Fluorine
Cerium	Radium	Helium
Chromium	Rhodium	Hydrogen
Cobalt	Rubidium	Iodine
Columbium	Ruthenium	Krypton
Copper	Scandium	Neon
Dysprosium	Sodium	Niton
Erbium	Silver	Nitrogen
Europium	Strontium	Oxygen
Gallium	Tantalum	Phosphorus
Gadolinium	Terbium	Selenium
Germanium	Thallium	Silicon
Glucinum	Thorium	Sulphur
Gold	Thulium	Tellurium
Holmium	Tin	Xenon
Indium	Titanium	
Iridium	Tungsten	
Iron	Uranium	
Lanthanum	Vanadium	
Lead	Ytterbium	
Lithium	Yttrium	
Magnesium	Zinc	
Manganese	Zirconium	
Mercury		
Molybdenum		

combines with hydrogen. For example, the negative radical of nitric acid, HNO_3 , is NO_3 . A negative radical must be combined with a positive radical before its valence is satisfied.

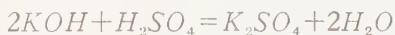
Salts are commonly prepared by treating a base with an acid, and as a result of the reaction which takes place water is also produced. For example, potassium hydroxide and hydrochloric acid react to form the salt potassium chloride and water; thus:



Potassium chloride is found to have neither the basic properties of potassium hydroxide nor the acid properties of hydrochloric acid; in fact, it does not affect litmus in any way. It is a neutral substance so far as acid or basic properties are concerned. When an acid and a base are brought together in the proper amounts to form a salt, they are said to *neutralize* each other.

75. Normal, Acid, Basic, and Mixed Salts.—The salts so far considered are those in which just enough metal is supplied to replace the hydrogen atoms in an acid; but there are other kinds. The following distinctions must, therefore, be made: A **normal salt** is a salt obtained from an acid by replacing all its hydrogen atoms by metal atoms. An **acid salt** is a salt obtained from an acid by replacing part of the hydrogen atoms by metal atoms. A **basic salt** is a salt obtained by the partial neutralization of a base by an acid. Following are equations showing the processes as used to produce the different kinds of salts:

A normal salt:



The resulting potassium sulphate, K_2SO_4 ,* is a normal salt, for all the hydrogen atoms in the acid have been replaced by potassium atoms.

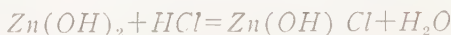
An acid salt:



*Potassium sulphate, K_2SO_4 , is formed at high temperatures, while the acid salt, $KHSO_4$, is formed at ordinary temperatures.

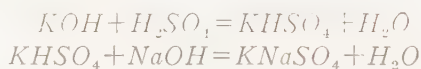
The resulting potassium hydrogen sulphate, $KHSO_4$, is an acid salt, for all the hydrogen atoms in the acid have not been replaced by potassium atoms.

A basic salt:



The resulting zinc hydroxy-chloride is a basic salt, for the base has been partly neutralized by the acid.

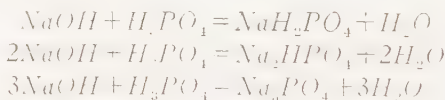
76. A **mixed salt** differs from a normal salt in that the hydrogen atoms in the acid have been replaced by two or more metals. For example, the mixed salt sodium potassium sulphate, $KNaSO_4$, can be made by first producing the acid salt potassium hydrogen sulphate and then treating this with sodium hydroxide, thus:



A mixed salt, also called a double salt, is formed by the replacement of the hydrogen atoms in an acid by different metals.

ACID SALTS, BASIC ACIDS, AND ACID BASES

77. Nomenclature of Acid Salts.—Different names are applied to acid salts in accordance with the number of hydrogen atoms that have been replaced by metals. For example, phosphoric acid, H_3PO_4 , can form three kinds of salts with sodium, depending on the number of sodium atoms that enter into the compound. Following are reactions showing the formation of the three salts formed by the action of phosphoric acid on sodium hydroxide:



The salt having the formula Na_3PO_4 is called *normal sodium phosphate*, because all of the hydrogen atoms in the acid have been replaced by sodium atoms. The other two salts formed, Na_2HPO_4 and NaH_2PO_4 , are acid salts, because only part of the hydrogen atoms in the acid have been replaced by sodium

atoms. Different names must be applied to them so that they can be distinguished from each other.

78. Based on the number of sodium atoms in the various salts, the following system of naming them is used:

NaH_2PO_4 = monosodium phosphate

Na_2HPO_4 = disodium phosphate

Na_3PO_4 = trisodium phosphate

Based on the number of hydrogen atoms in the various salts, the following system of names is used:

NaH_2PO_4 = dihydrogen sodium phosphate

Na_2HPO_4 = monohydrogen sodium phosphate

Na_3PO_4 = normal sodium phosphate

Following is another set of names that is sometimes used:

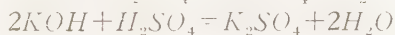
NaH_2PO_4 = primary sodium phosphate

Na_2HPO_4 = secondary sodium phosphate

Na_3PO_4 = tertiary sodium phosphate

The name *sodium phosphate* is usually applied to Na_2HPO_4 , for this salt is the most common of the three.

79. Some acids, like sulphuric acid, form but one acid salt with a metal. For example, potassium hydroxide can react with sulphuric acid in the following ways:

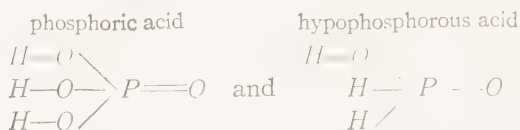


The normal salt, K_2SO_4 , is called *potassium sulphate*. The acid salt is called *acid potassium sulphate* or *potassium hydrogen sulphate*. No other names are necessary, as in the case of the sodium phosphates, for there is but one acid potassium sulphate. Acid potassium sulphate is sometimes called potassium bisulphate or potassium disulphate to show that twice as much SO_4 radical is present as is needed to form a normal salt with the potassium contained.

80. Basicity of Acids.—All the hydrogen atoms in the acids so far considered can be replaced by metals. There are a few acids, however, in which but part of the hydrogen atoms can be replaced and in order to explain more clearly why only

certain of the hydrogen atoms are replaced, graphic or structural formulas, in which the valence of the different atoms is indicated by means of dashes, will be used.

Consider the two oxyacids (acids containing oxygen), phosphoric acid, H_3PO_4 , and hypophosphorous acid, H_3PO_2 , the graphic or structural formulas of which are, respectively:



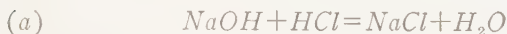
In these formulas the valence of each atom is indicated as follows: Hydrogen is always monovalent in any compound, therefore each hydrogen atom is shown, connected by one *bond*, or dash, to an oxygen or phosphorus atom. Oxygen is always bivalent and each atom is therefore shown connected once to hydrogen and once to phosphorus, thus satisfying its valence of 2. In each formula, however, one oxygen atom must be written with a double bond in order to show its valence of 2. Phosphorus in phosphoric acid is pentavalent and is shown connected twice to one oxygen and once to each of three oxygens, thus satisfying its valence of 5. The three hydrogen atoms of phosphoric acid are replaceable, the graphic formula is therefore written to show that each hydrogen atom is connected, but only one of the hydrogen atoms of hypophosphorous acid is replaceable. The first acid contains three hydroxyl, OH , groups and the latter but one. Investigations showed that only hydrogen atoms in the hydroxyl groups of oxyacids are replaceable by metals and that those hydrogen atoms of oxyacids that are not in the hydroxyl groups are not replaceable by metals. These facts do not, of course, apply to acids that do not contain oxygen. The hydrogen atoms in acids like hydrochloric acid, HCl , and hydrofluoric acid, HF , can be entirely replaced by metal.

81. An acid that requires 1 atom of a univalent metal to replace all the *replaceable* hydrogen in 1 molecule of it is said to be *monobasic acid*. An acid that requires 2 atoms of univalent metal or 1 atom of a divalent metal to replace all the

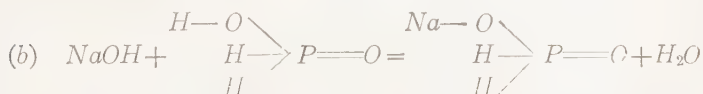
replaceable hydrogen atoms in 1 molecule of it is said to be *dibasic*. An acid that requires 3 atoms of a univalent metal or 1 atom of a trivalent metal to replace all of the replaceable hydrogen atoms in 1 molecule of it is said to be *tribasic*. The basicity of an oxyacid, as shown before, is limited by the number of hydroxyl groups it contains; all the hydrogen atoms in acids that do not contain oxygen are replaceable by metals. The term **basicity** is used because the metals that replace the hydrogen in acids are usually obtained from bases.

82. Examples of Reactions Between Bases and Acids.—The following examples will serve to make the conception of the basicity of acids clear:

Monobasic acids:

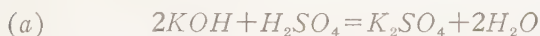


Hydrochloric acid is monobasic because 1 molecule of the base, sodium hydroxide, is needed to supply the 1 atom of univalent sodium required to replace the hydrogen atom in one of its molecules.

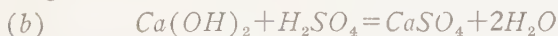


Hypophosphorous acid is monobasic because 1 molecule of the base, sodium hydroxide, is needed to supply the 1 atom of univalent sodium required to replace the replaceable hydrogen atom in 1 molecule of it.

Dibasic acids:



Sulphuric acid is dibasic because 2 molecules of the base, potassium hydroxide, are needed to supply the 2 atoms of univalent potassium required to replace the replaceable atoms of hydrogen in 1 molecule of it.



Sulphuric acid is shown to be dibasic by this reaction also, because 1 molecule of the base, calcium hydroxide, is needed to supply the 1 atom of divalent calcium required to replace the replaceable hydrogen atoms in 1 molecule of it.

Tribasic acids:



Phosphoric acid is tribasic because 3 molecules of the base, sodium hydroxide, are needed to supply the 3 atoms of univalent sodium required to replace the replaceable hydrogen atoms in 1 molecule of it.



Phosphoric acid is shown to be tribasic by this reaction also, because 1 molecule of the base, aluminum hydroxide, is needed to supply the 1 atom of trivalent aluminum required to replace the replaceable hydrogen atoms in 1 molecule of it.

83. Acidity of Bases.—Bases are classed according to the number of hydrogen atoms that can be replaced in an acid by 1 molecule of the metal supplied. For example, sodium hydroxide, NaOH , is a *monacid base*, because each molecule of it supplies 1 atom of univalent sodium, capable of replacing 1 hydrogen atom in an acid. Calcium hydroxide, $\text{Ca}(\text{OH})_2$, is a *diacid base*, because each molecule of it supplies 1 atom of divalent calcium, capable of replacing 2 hydrogen atoms in an acid. Aluminum hydroxide, $\text{Al}(\text{OH})_3$, is a *triacid base*, because each molecule of it supplies 1 atom of trivalent aluminum, capable of replacing 3 hydrogen atoms in an acid. The reactions used to exemplify the basicity of acids should be studied in connection with the acidity of bases, for they show how monacid, diacid, and triacid bases react with acids.

COMPOUNDS CONTAINING TWO ELEMENTS

84. Binary Compounds.—Compounds that consist of two elements, or two groups acting as elements, are called **binary compounds**. The ending *ide* is applied to these substances. In Table VIII are shown a few examples of binary compounds and the system of naming them. In each case, the ending *ide* is applied to the less positive or the negative elements; usually, a non-metal. The more positive element, usually a metal, is written before the less positive or negative element.

85. In some cases an element can unite with another element to form more than one compound. There is a system of naming these substances so that they can be distinguished from one another. For example, iron may unite with chlorine to form two different kinds of chlorides, depending on the number of atoms of chlorine joined to 1 atom of iron; or, depending on the valence of the iron in each chloride. The chloride $FeCl_2$, in which iron is divalent and in which but 2 atoms of chlorine are present to every atom of iron, is called *ferrous chloride*. The substance $FeCl_3$, in which iron is trivalent and

TABLE VIII
NOMENCLATURE OF BINARY COMPOUNDS

Positive Element	Negative Element	Formula	Name of Binary Compound
Magnesium	Oxygen	MgO	Magnesium oxide
Zinc	Sulphur	ZnS	Zinc sulphide
Potassium	Bromine	KBr	Potassium bromide
Calcium	Carbon	CaC_2	Calcium carbide
Sodium	Chlorine	$NaCl$	Sodium chloride
Hydrogen	Sulphur	H_2S	Hydrogen sulphide
Hydrogen	Chlorine	HCl	Hydrogen chloride
Lead	Iodine	PbI_2	Lead iodide
Ammonium	Chlorine	NH_4Cl	Ammonium chloride

in which 3 atoms of chlorine are present to every atom of iron, is called *ferric chloride*. In other words, the ending *ous* is added to the name of the positive element, usually a metal, to show that it is present with the lower valence and that it is combined with a lower amount of negative element than in the compound in which the positive element has the ending *ic*.

Following are a few examples showing the use of the endings *ous* and *ic*:

Cu_2O , cuprous oxide	CuO , cupric oxide
$SnCl_2$, stannous chloride	$SnCl_4$, stannic chloride
CrO , chromous oxide	Cr_2O_3 , chromic oxide

86. Elements Uniting in More Than One Proportion.—Another method, in which a prefix is attached to the negative element, is used to distinguish binary compounds formed by elements uniting in more than one proportion. The prefixes *mono*; *di*, or *bi*; *tri*; *tetra*; and *penta* are applied to show whether the number of atoms of the negative element present is, respectively, one, two, three, four, or five. Following are a few examples of this system:

CO , carbon monoxide	CO_2 , carbon dioxide
SO_2 , sulphur dioxide	SO_3 , sulphur trioxide
PCl_3 , phosphorus trichloride	PCl_5 , phosphorus pentachloride
H_2O , hydrogen monoxide	H_2O_2 , hydrogen dioxide

The prefix *per* is sometimes applied to the negative element to show that the greatest possible number of atoms of the negative element is present, thus:

H_2O_2 , hydrogen peroxide, known also as hydrogen dioxide

PbO_2 , lead peroxide, known also as lead dioxide

Na_2O_2 , sodium peroxide, known also as sodium dioxide

There is no compound of hydrogen and oxygen in which there is a greater proportion of the negative element than in hydrogen peroxide. The same fact holds true for all other binary compounds in which the prefix *per* appears.

The following oxides of nitrogen are excellent examples of substances that follow the nomenclature explained in the foregoing:

N_2O , nitrous oxide

NO , nitric oxide

N_2O_3 , nitrogen trioxide

NO_2 or N_2O_4 , nitrogen dioxide or nitrogen tetroxide

N_2O_5 , nitrogen pentoxide

The prefix *sesqui* is sometimes added to the negative element to denote that there is present $1\frac{1}{2}$ atoms of the negative element to every atom of the positive element. For example, Fe_2O_3 , ferric oxide, is sometimes called *iron sesquioxide*.

NOMENCLATURE OF ACIDS AND SALTS BELONGING TO
ONE SERIES

87. Series of Acids.—The system of naming acids and salts should be studied carefully, for it is used in every phase of chemistry. Some acids so far considered have names ending in *ic*. Others end in *ic*, but have in addition the prefix *hydro*; others, again, have different prefixes and suffixes. Each one of them is, however, based on the same system of naming substances.

An acid is generally named by referring to its characteristic element. It should be borne in mind, however, that in an acid neither hydrogen nor oxygen can be considered as a characteristic element, for the former is found in all and the latter in most acids. For example, H_2SO_4 is called sulphuric acid, and HNO_3 , nitric acid, being named with reference to the respective characteristic elements sulphur and nitrogen.

The principal acid of a series takes the ending *ic*, as $HClO_3$, *chloric acid*; the next acid in the series, containing less oxygen than the principal acid, takes the ending *ous*, as $HClO_2$, *chlorous acid*; the acid containing even less oxygen than the acid ending in *ous*, takes the ending *ous* and the prefix *hypo*, as $HClO$, *hypochlorous acid*; the acid of the series containing hydrogen and the characteristic element only, takes the ending *ic* and the prefix *hydro*, as HCl , *hydrochloric acid*. If there is an acid in the series containing more oxygen than the principal acid, it has the ending *ic* and the prefix *per*, as $HClO_4$, *perchloric acid*.

Following is a summary of the formulas and names of the acids of chlorine:

HCl , *hydrochloric acid*
 $HClO$, *hypochlorous acid*
 $HClO_2$, *chlorous acid*
 $HClO_3$, *chloric acid*
 $HClO_4$, *perchloric acid*

88. The foregoing names have been used for years. There is also a set of names, based on scientific grounds, that can

properly be used to designate the various chlorine acids, as follows:

HCl , hydrogen *chloride*
 $HClO$, hydrogen *hypochlorite*
 $HClO_2$, hydrogen *chlorite*
 $HClO_3$, hydrogen *chlorate*
 $HClO_4$, hydrogen *perchlorate*

89. Series of Salts.—The names of salts depend on the names of the acids from which they are formed. A salt formed by a metal and the negative radical of an oxyacid ending in *ic* has the ending *ate*; and a salt consisting of a metal and the negative radical of an oxyacid ending in *ous* has the ending *ite*. The prefix appearing in the name of the acid is retained in the name of the salt. As has been explained before, names of salts consisting of but two elements end in *ide*, even though the acid has the prefix *hydro* and the suffix *ic*. Names of salts of chlorine acids receive the same endings as the acids, as shown in the foregoing explanations, excepting that the name of the metal in the salt is used instead of hydrogen. Following are the names of different salts formed when potassium hydroxide reacts with the acids of chlorine:

KCl , potassium *chloride*; formed from HCl , *hydrochloric* acid.

$KClO$, potassium *hypochlorite*; formed from $HClO$, *hypochlorous* acid or hydrogen *hypochlorite*.

$KClO_2$, potassium *chlorite*; formed from $HClO_2$, *chlorous* acid or hydrogen *chlorite*.

$KClO_3$, potassium *chlorate*; formed from $HClO_3$, *chloric* acid or hydrogen *chlorate*.

$KClO_4$, potassium *perchlorate*; formed from $HClO_4$, *perchloric* acid or hydrogen *perchlorate*.

90. Salts containing positive elements that exhibit more than one valence are named in much the same way as binary compounds containing positive elements that have more than one valence. The name of the positive element, when it has the lower valence, takes the ending *ous*, and, when it has the higher valence, takes the ending *ic*. Thus:

SnSO_4 , stannous sulphate

$\text{Sn}(\text{SO}_4)_2$, stannic sulphate

Each salt is a *sulphate*, for each of them contains the negative radical, SO_4 , of sulphuric acid. The salt in which tin is divalent is called *stannous sulphate*, and the one in which it is tetravalent is called *stannic sulphate*.

91. Formulas and Names of Some Common Acids and Salts.—The general application of the nomenclature explained in the preceding pages is shown in the succeeding list of chemical compounds, for each of which the formula is given and the corresponding name:

H_2S , hydrogen sulphide

HCl , hydrochloric acid, or hydrogen chloride

HNO_3 , nitric acid, or hydrogen nitrate

H_3PO_4 , phosphoric acid, or hydrogen phosphate

H_2SO_3 , sulphurous acid, or hydrogen sulphite

Cu_2O , cuprous oxide

CuO , cupric oxide

HgCl_2 , mercuric chloride, or mercury bichloride

Hg_2Cl_2 , mercurous chloride

FeSO_4 , ferrous sulphate

$\text{Fe}_2(\text{SO}_4)_3$, ferric sulphate

FeSO_3 , ferrous sulphite

$\text{Fe}_2(\text{SO}_3)_3$, ferric sulphite

NaClO_4 , sodium perchlorate

SnCl_2 , stannous chloride

$\text{Ca}(\text{ClO}_3)_2$, calcium chlorate

SO_2 , sulphur dioxide

SO_3 , sulphur trioxide

Cu_2S , cuprous sulphide

CuS , cupric sulphide

NaHSO_4 , sodium bisulphate, acid sodium sulphate, or sodium hydrogen sulphate

NaHCO_3 , acid sodium carbonate, sodium hydrogen carbonate, or sodium bicarbonate

KCN , potassium cyanide

$\text{Ca}(\text{ClO})_2$, calcium hypochlorite

INORGANIC CHEMISTRY FOR PHARMACY STUDENTS

(PART 2)

HYDROGEN, OXYGEN, NITROGEN, CARBON, AND THEIR COMPOUNDS

INTRODUCTION

MEASUREMENT OF GAS PRESSURE. LIQUEFACTION OF GASES

1. Measurement of Pressure.—Throughout the subject of chemistry, and especially when gases are considered, expressions such as the following are often met with: *Distillation under diminished pressure*; *distillation in vacuo*; and *760 millimeters pressure*. As it is important that the meaning of these expressions should be understood, they will be explained by means of Fig. 1.

In Fig. 1 is shown a barometer of the form commonly used in laboratories when making distillations at pressures less than that of the atmosphere. At sea level the average pressure exerted by the atmosphere is equal to 14.7 pounds per square inch, and this pressure corresponds with that required to support a column of mercury, 760 millimeters in height, in a vertical, exhausted tube.

2. The apparatus, represented in Fig. 1, consists of a bent glass tube, sealed at the upper end and fitted with a stop-cock *g* at the other end; this end is joined to a short tube *e f*.

If the ends *e*, *f* and the stop-cock *g* are left open, the pressure exerted upon the lower end of the mercury column is that of the atmosphere. If now a vacuum pump is attached to the end *f*, after the end *e* has been closed, the distance between the two ends, or levels, of the mercury column, which is normally equal to 760 millimeters, will gradually decrease and the ends may shortly occupy the positions indicated by the lines *a b* and *c d*. This position, may, for instance, correspond to a pressure of 600 millimeters.

Continuing the operation of the vacuum pump, the levels of the mercury columns in the two limbs *j* and *k* tend to approach each other as zero pressure is reached.

In commercial instruments, a scale graduated in millimeters, similar to that shown at *h i*, is employed. This scale may be adjusted so that its zero point is on the same level as that of the lower end of the mercury column, thus allowing the height of the column to be read off directly on the scale.

In laboratory work the end *e* of the barometer is connected to the vessel or apparatus in which a given reduction of pressure is to be produced, the barometer indicating when the desired pressure has been reached.

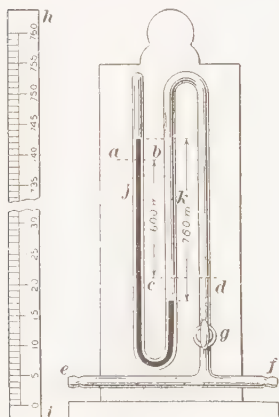


FIG. 1

3. Liquefaction of Gases.—As reference is occasionally made to *liquefied gases*, a brief explanation

will be made of the process by which liquefaction of gases is produced.

Under atmospheric pressure, a great many substances may be either gaseous, liquid, or solid, depending on the prevailing temperature. For instance, water is liquid below a temperature of 100° C. and is gaseous above it; alcohol is liquid below 78° C. and is a vapor above it; sulphur dioxide boils at -8° C., and, if it were impossible to reduce the temperature below 0° C., would only be known as a gas.

4. When the temperature of a gas is sufficiently reduced and the gas is subjected to a high pressure, there is a tendency for it to liquefy. Faraday was among the first of the early experimenters to liquefy ammonia, chlorine, and carbon dioxide by cooling and compressing the gases simultaneously. The apparatus employed by him was very simple, consisting merely of a piece of thick-walled glass tubing, bent and sealed as shown in Fig. 2. The materials necessary for the formation of the gas were placed in the tube, which was then sealed. The limb *d* was immersed in a freezing mixture, such as ice and NaCl , or ice and calcium chloride, depending upon the temperature desired, while the limb *c* was heated. If, for instance, the limb *c* contained sodium carbonate, the carbon dioxide



FIG. 2

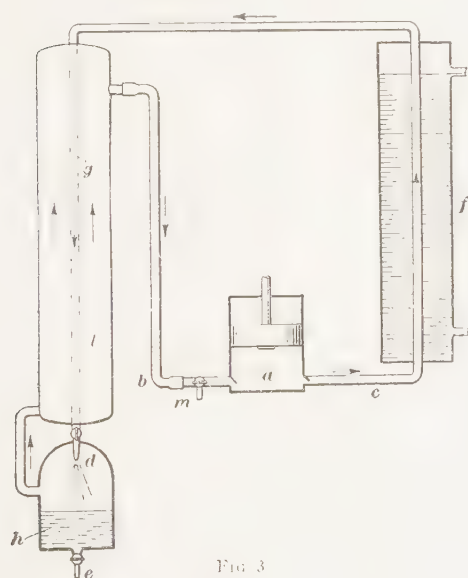


FIG. 3

liberated upon heating was condensed to a liquid in *d*. The diagrammatic sketch, Fig. 3, illustrates the principles involved and the general method of procedure followed in the liquefaction of gases.

5. The pump *a*, Fig. 3, draws air or gas through the branch pipe *m* into the apparatus. When a sufficient quantity has been obtained, this branch is closed by means of the valve, shown at the junction of the pipes. The pump, which is able to exert a

pressure of about 50 atmospheres, or about 730 pounds per square inch, forces the gas into the tube *c* in the direction of the arrows and it escapes, eventually, through the orifice *d* into the receiver *h*.

The heat, developed by the compression of the gas in the pump, is removed from the gas while passing through the tube *c*, the first portion of this tube being cooled by the water-jacket *f*. The temperature of the gas is also lowered, as a result of its expansion, on leaving the orifice *d*, and a further reduction of temperature takes place as the gas expands on entering the large tank *l*. The cooled gas serves now as a means for cooling the gas descending through the tube *g*, which is again cooled by reason of its expansion into *h*. As the gas is continually passing through the apparatus its temperature is gradually reduced, until finally the *critical temperature* is reached and the gas condenses. The liquid gas may be drawn off through the tube *e*.

6. By the term **critical temperature** is meant the temperature *below* which a gas will condense and become liquid, and *above* which temperature no amount of pressure will cause it to liquefy.

The pressure at which the critical temperature is just sufficient to cause the gas to liquefy, is known as the **critical pressure**. At temperatures *below* the critical temperature, the pressure necessary to liquefy a gas is *less* than the critical pressure.

HYDROGEN

Symbol H. Atomic weight 1.008. Molecular weight 2.016. Valence I.

7. Occurrence.—Hydrogen constitutes about one-ninth the weight of water, the balance being oxygen; it is an essential constituent of all acids. It also occurs in organic matter, such as petroleum, animal and vegetable materials, etc., combined with carbon, oxygen, nitrogen, and sulphur in various proportions. Free hydrogen, while found in some volcanic

gases, forms but a very small part of the hydrogen total. The air contains practically no free hydrogen.

8. Methods of Preparation of Materials.—Before describing the preparation of hydrogen, it may be well to state that there are two ways of preparing materials, so far as the chemist is concerned: The *laboratory*, or experimental, method and the *technical*, or commercial, method. The laboratory method is confined to the preparation of small quantities for use in the laboratory, while the technical method is used to produce large amounts for industrial purposes. Experience has shown that laboratory methods are not always satisfactory

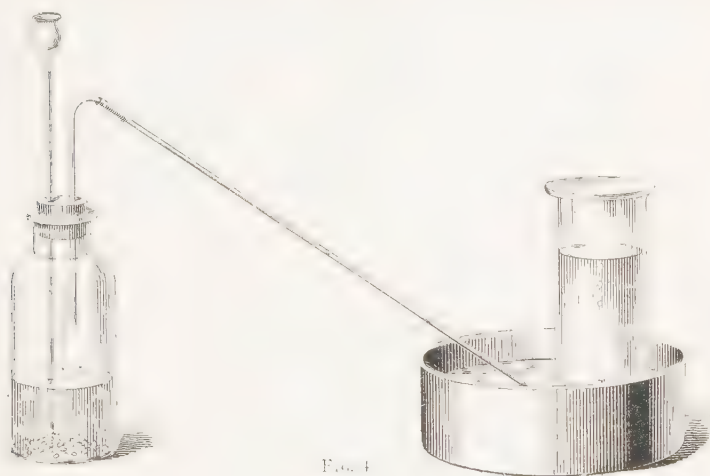


FIG. 4

when used as technical methods, on account of the cost, unsatisfactory condition of the products, mechanical difficulties, etc. On the other hand, many laboratory methods have been reproduced successfully on a large scale.

9. Laboratory Preparation of Hydrogen.—The most satisfactory laboratory method of obtaining hydrogen is by replacing the hydrogen in acids by a metal. Usually, hydrochloric acid or sulphuric acid and iron or zinc are used to produce this change. Fig. 4 shows how the gas is collected. Some metal, usually zinc, is placed in the bottle on the left and a two-holed stopper is fixed into the neck of the bottle; a thistle

tube is inserted through one hole and lowered until it is about $\frac{1}{4}$ inch from the bottom of the bottle. A bent tube is passed

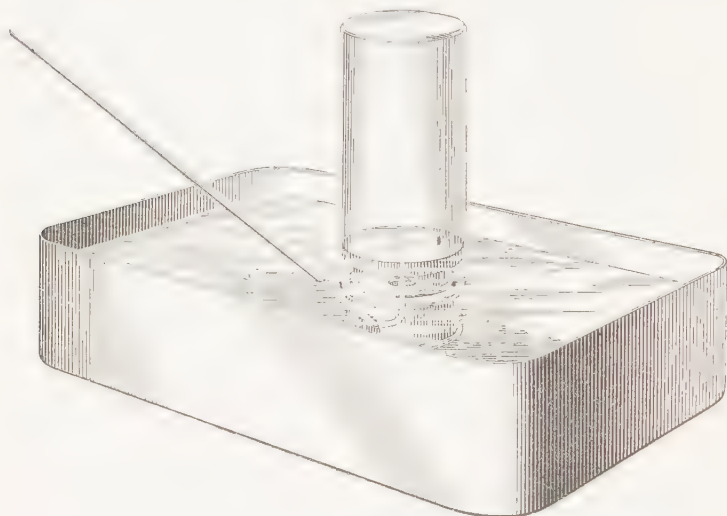


FIG. 5

through the other hole and connected to a delivery tube by a piece of rubber tubing, which should fit tightly. The other end of this tube is arranged as shown in Fig. 4. The inverted bottle, shown in Figs. 4 and 5, is supported in the water on a *beehive shelf*, shown enlarged in Fig. 6. The delivery tube passes through the opening in the side of the shelf. Either a basin or pan may be used to hold the water, as shown in Figs. 4 and 5, respectively. Water is used in the inverted bottle so that the gas, when collected above it, will be pure. As the

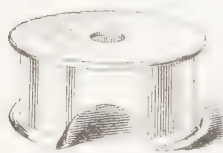


FIG. 6

gas passes through the water it displaces it, as shown in Fig. 4, and is obtained in a pure state. If water were not in the bottle, the gas would mix with the air in the bottle and would not be pure. The collecting bottle is filled to the top with water and the hand placed over the mouth of the bottle to prevent loss of any of the water. The bottle is then inverted into the basin filled with water, and the hand removed when the neck of the bottle is below the surface of the water.

The apparatus should not leak, for the entrance of air into the apparatus may cause the formation of a hydrogen-air mixture that explodes. One can tell whether everything is air-tight by wetting all connections and blowing through the apparatus. The appearance of bubbles at any connection indicates a leak at that point.

10. After the apparatus is arranged as shown in Fig. 4, dilute sulphuric acid—made by slowly adding 1 part, by volume, of the concentrated acid to 6 parts of water—is gradually poured down the thistle tube until the surface of the acid in the generating flask is above the lower end of the thistle tube. To avoid accidents, *water* is never *added* to concentrated sulphuric acid.

Hydrogen is generated upon the addition of the acid to the metal and is carried over into the inverted bottle. Too much acid must not be added at one time, lest the chemical change takes place too rapidly and the mixture becomes too hot. If this does occur, a little water poured into the thistle tube and around the outside of the flask will cool it.

Care is taken to expel all the air from the apparatus before collecting the gas. The collecting bottle is not put into place until the hydrogen has driven out all of the air from the generating flask and connecting tube. Whether this is the case can be found by filling a test tube with water, inverting it in the basin containing water, and collecting some of the gas. A flame is then brought to the mouth of the tube filled with gas to note whether the hydrogen burns quietly. (All vessels containing hydrogen are held with the opening *downwards* to prevent the escape of the gas, for it is lighter than air.) If all the air has been driven out of the apparatus, the gas will burn quietly in the test tube, which indicates that the gas may be collected.

11. Reactions.—The chemical change that takes place when sulphuric acid acts on zinc can be represented by a chemical equation. As it is necessary to know how to write chemical equations, a consideration of the subject at this point will be helpful.

Tests have shown that zinc and sulphuric acid react chemically to form hydrogen and zinc sulphate. It has also been determined by tests that every 65.37 parts by weight of zinc react with 98.076 parts of sulphuric acid to form 2.016 parts by weight of hydrogen and 161.43 parts of zinc sulphate. The question naturally arises as to whether the rules given in the preceding Section can be followed in writing a chemical equation that will represent the reaction taking place.

As already stated, a chemical equation, to be correct, must represent a change that actually takes place and one that can be reproduced by either a laboratory or by a technical method. In other words, equations mathematically correct are not always chemically correct; they must represent real changes and not imaginary ones.

12. The valence of elements in a reaction affords an excellent help in writing chemical equations. For example, there are in 1 molecule of sulphuric acid 2 replaceable hydrogen atoms of hydrogen, each of which has a valence of 1; these atoms can be replaced by either 2 atoms of a univalent metal or 1 atom of a divalent metal. As zinc is a divalent metal, only 1 atom of this element is needed to free the 2 univalent atoms of hydrogen from the acid. The left side of the equation will therefore, be:



Tests have also shown that zinc sulphate and hydrogen are formed in this change. It, therefore, remains to determine how many molecules of each are produced. One zinc atom can produce but 1 molecule of zinc sulphate when it is acted on by sulphuric acid; likewise, 1 molecule of sulphuric acid can form but 1 molecule of hydrogen. The complete equation is, therefore,



It will be observed that the hydrogen in the equation is written 2H and not H_2 , as it should be, if the theory regarding the atomicities of molecules is taken into consideration. The reason for this apparent contradiction of the theory may be explained as follows: Hydrogen may exist in two forms, *nascent* and *molecular*. Nascent hydrogen is written 2H and

the molecular hydrogen, H_2 . Nascent hydrogen exists, as such, only momentarily and almost immediately changes to the molecular form. While in the active or nascent state, however, the element exhibits much greater chemical activity than when in the molecular form.

It should be remembered, however, that nascent hydrogen has never been isolated and that the preceding explanation is purely theoretical; but it is based upon the fact that hydrogen produced under certain conditions is more active than that produced under other conditions, and in order to distinguish the more active form, it is called **nascent hydrogen**.

The equation shows that 1 atom, or 1 molecule, of zinc (each molecule contains 1 atom) is acted on by 1 molecule of sulphuric acid to form 1 molecule of hydrogen.

The sum of the relative weights on the left side is 65.37 for zinc plus 98.076 for sulphuric acid, or 163.446 for both. That on the right is 2.016 for hydrogen plus 161.43 for zinc sulphate, or 163.446 for both. Every equation must be written so that the sum of the relative weights on each side of the equation is the same. If an excess of sulphuric acid is added to 65.37 grammes of zinc, only 98.076 grammes of acid take part in the change, the excess being unaffected. It is also found by weighing the products that 2.016 grammes of hydrogen and 161.43 grammes of zinc sulphate are formed.

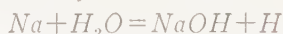
If the foregoing plan is followed in writing and verifying the accuracy of chemical equations, the work will be greatly simplified. But it must be remembered that a correct equation must comply with the following requirements: *A chemical equation must represent a true chemical change; the materials used and formed must be known; the number of atoms of any element on one side of the equation must be the same as the number of atoms of that element on the other side; the sum of the relative weights on each side of the equation must be equal.*

13. Preparation of Hydrogen From Water.—Many metals can, under the proper conditions, displace hydrogen from water. Only the active metals like sodium, potassium, and calcium can, however, displace it from cold water with any

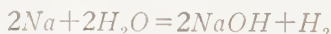
degree of rapidity. Sodium may conveniently be used to prepare hydrogen from water.

A very small piece of sodium, about half the size of a pea, is placed in a basin filled with water. This operation is best accomplished by wrapping the sodium in a piece of filter paper by means of a pair of tongs; the metal should never touch the moist fingers. The sodium will appear to burn, will heat up the paper and cause it ignite. This heat is produced when the chemical change between water and sodium takes place. It must be remembered that *in order to avoid explosions, only very small quantities of sodium are used at a time*. After action has ceased, there is no sodium left. This can be explained by considering the chemical change that takes place.

Sodium has a greater attraction than hydrogen for oxygen; that is, the *chemical affinity* between sodium and oxygen is greater than that between hydrogen and oxygen. The sodium can, therefore, take oxygen from the hydrogen in water. It has been found by experiment that sodium replaces but half the hydrogen in each molecule of water, forming hydrogen and a substance called sodium hydroxide. The reaction is, therefore,



This equation does not, however, show the change that actually takes place, for hydrogen is always found in the molecular state, H_2 , not as an atom, H . To show the hydrogen as a molecule, the equation should be

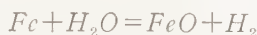


This equation shows that 2 atoms, or molecules, of sodium (for each molecule contains but 1 atom) react with 2 molecules of water to form 2 molecules of sodium hydroxide and 1 molecule of hydrogen. The hydrogen gas, which passes off, can be collected, while the sodium hydroxide remains in solution. A change, such as this one, in which an atom of sodium is substituted in a molecule of water for an atom of hydrogen, is called **substitution**.

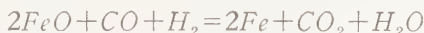
14. Technical Production of Hydrogen.—The methods of preparing hydrogen, so far described, are for laboratory use. Within the last few years the commercial

uses of hydrogen have been extended until its production has become an important industrial factor. There are now several successful technical methods of manufacturing hydrogen of which the following will be considered in detail: (a) Iron-steam process, (b) Linde-Frank-Caro process, and (c) electrolytic process.

(a) *Iron-Steam Process*.—As previously stated, most metals can, under proper conditions, free hydrogen from oxygen in water. If iron, *Fe*, for example, is heated to 800°C . and steam is passed over it, hydrogen and ferrous oxide are formed, as shown by the equation:



The hydrogen is collected and the ferrous oxide is changed back into iron, so that it can be used over again, by subjecting it to the action of *water gas*, which consists of about 50 per cent. of hydrogen, 40 per cent. of carbon monoxide, *CO*, and 10 per cent. of impurities. The change that takes place when ferrous oxide is acted on by water gas is shown in the equation:



In this equation it is shown that for every 2 molecules of ferrous oxide used, 1 of hydrogen and 1 of carbon monoxide are needed, and that 2 molecules of iron (each molecule of iron contains 1 atom), 1 of carbon dioxide, and 1 of water are formed.

(b) *Linde-Frank-Caro Process*.—This process depends upon the fact that carbon monoxide and hydrogen liquefy at different temperatures. Water gas, which consists mainly of carbon monoxide and hydrogen, is cooled and compressed until the carbon monoxide changes to a liquid, leaving the hydrogen in a gaseous form. Carbon monoxide becomes a liquid at a temperature of -192°C ., while hydrogen remains a gas until a temperature of -253°C . is reached. The water gas is made by passing steam over red-hot coke. The reaction is as follows:



Each molecule of water or steam is converted by one of carbon into one molecule of carbon monoxide and one of hydrogen.

(c) *Electrolytic Production of Hydrogen.*—In this process water is broken up into its constituent elements, hydrogen and oxygen, by the aid of an electric current. The details of this method of decomposing water will be described in another Section. The electrolytic process is probably the most suitable of all methods for use in small plants, for it is easy to operate, requires but little attention, and is not expensive. Hydrogen is also made, as will be shown later, during the production of sodium hydroxide, $NaOH$, by the electrolysis of a water solution of sodium chloride, $NaCl$.

15. Properties of Hydrogen.—A study of the hydrogen made by any of the above methods shows that it has neither color, taste, nor odor. It is the lightest gas known, having a specific gravity of .0696 (air=1). Hydrogen is absorbed mechanically by many metals, as, for example, heated iron, gold, palladium, and finely divided platinum. Some doubt exists in the case of palladium as to whether some of the hydrogen is not combined chemically as well as mechanically occluded by the metal.

Chemically, hydrogen is an active element and acts in many respects like metals. While burning, it unites with oxygen to form an exceedingly hot flame, water being produced. If this flame is allowed to play on a piece of calcium oxide, commonly called quicklime, it yields a dazzling white light, generally known as *calcium*, or *limelight*.

Hydrogen usually ignites with a small explosion, which sounds not unlike that heard when a bottle is uncorked. This fact serves as one means of identifying the gas, when it is mixed with oxygen.

Under ordinary conditions, and temperature, the chemical action between hydrogen and oxygen is very slow. Above $600^{\circ} C.$, however, hydrogen has a marked affinity for oxygen and unites with it rapidly. It also has a strong attraction for chlorine. In fact, the attraction existing between hydrogen and oxygen or chlorine is so strong that hydrogen can replace many elements with which oxygen or chlorine may be combined.

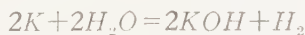
Finely divided platinum can produce chemical action between hydrogen and oxygen by its mere presence; it acts by contact, is unaffected when the chemical change is completed, and may therefore be called a catalytic agent. In contact with a large volume of hydrogen and oxygen, platinum causes the gases which are nearest to it to unite, with the evolution of heat. This in turn causes the rest of the mixture to combine. Gas lighters and some automatically lighting gas jets are based on this principle.

TABLE I
RELATIVE CHEMICAL ACTIVITY
OF METALS

16. Relative Activity of Metals and Hydrogen.—Hydrogen, which acts

chemically like metals (these will be considered in another Section), possesses greater chemical activity than some metals and less than others. Table I shows the relative activity of the common metals and hydrogen. All the metals more active than hydrogen, that is, all the metals from potassium to lead, can replace hydrogen in dilute acids, and, in some cases, in water; the metals from antimony to gold,

however, cannot replace hydrogen in dilute acids or water. For example, potassium replaces hydrogen in water with great activity, as shown in the equation:



Sodium replaces hydrogen in water in a similar way, but the action is not as vigorous as in the case of potassium. Magnesium can replace a small amount of hydrogen from boiling water and a larger amount from superheated steam. Zinc can replace hydrogen in dilute acids, as shown in the equation:

Most Active Metals	Least Active Metals
Potassium	Antimony
Sodium	Bismuth
Calcium	Copper
Magnesium	Mercury
Aluminum	Silver
Chromium	Platinum
Manganese	Gold
Zinc	
Iron	
Nickel	
Tin	
Lead	
Hydrogen	



Metals from antimony to gold, as shown in the table, cannot replace hydrogen from either dilute acids or water.

This table of relative activity of metals is well worth remembering, for the relation holds good, as will be shown later, for many other chemical reactions.

17. Uses of Hydrogen.—It is only since 1907 that hydrogen has become a commercially important material. Today, it is indispensable in several industrial operations. Probably the most important of all uses is in oxyhydrogen burners. If a jet of oxygen is passed into a flame of hydrogen, a temperature of $2,800^\circ \text{C.}$ is obtained. Fig. 7 shows how the gases are mixed in the operation of oxyhydrogen burners without danger of explosion. The oxygen supply is connected with the tube *O* and the hydrogen supply with the tube *H*. After the hydrogen is ignited, the oxygen is gradually introduced.

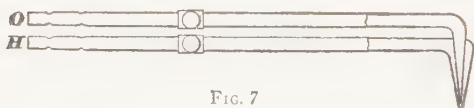


FIG. 7

In the nozzle shown in Fig. 7 there is no danger of an explosion, as a result of a backward rush of the gases, for the hydrogen and oxygen come into contact only at the point where the burning takes place. One part of oxygen to 4 parts of hydrogen, by volume, is found to give satisfactory results.

The oxyhydrogen burner is used where high temperatures are necessary to produce the desired results. It is used to fuse and weld platinum and to unite the edges of lead sheets for making vessels to hold acids. The oxyhydrogen flame is needed to prepare laboratory apparatus from fused quartz. The washed quartz sand is melted by the oxyhydrogen flame and molded into the desired shape. Quartz glass will resist the action of all acids, excepting hydrofluoric and phosphoric. It expands very little when subjected to the action of heat and does not, therefore, crack very readily. The oxyhydrogen flame is also used to cut heavy steel plates.

18. Hydrogen is used in the manufacture of tungsten-filament lamps to form an atmosphere free from oxygen. A

mixture of hydrogen and nitrogen, containing equal parts by volume of both, is employed when the filaments are brought to a high temperature during their final treatment. No gas or mixture of gases, such as air, that will react chemically with tungsten can be used during this operation.

Owing to its very low density, hydrogen is used in balloons and dirigible airships. The load that a balloon will carry up is equal to the difference between the weight of the balloon with the contained hydrogen and the weight of the air displaced. One liter of hydrogen can lift 1.2 grammes.

A very extensive and important use for hydrogen has developed in the fat industry within recent years. The introduction of hydrogen into soft fatty and oily bodies of low melting points, such as cottonseed oil, converts them in the presence of finely divided nickel, which acts as a *catalytic* agent, into hard fats of higher melting points. The hard fats are suitable for use in the manufacture of soap, candles, and oleomargarine, and for cooking purposes, even though the soft, easily melting fats cannot be used for these purposes with the same degree of satisfaction. The process of introducing hydrogen into the molecules of the liquid or easily melted soft fats is called **hydrogenation**.

OXYGEN

PROPERTIES, PREPARATION, AND COMBINATIONS

Symbol O. Atomic weight 16. Molecular weight 32. Valence II.

19. Occurrence.—Oxygen is the most abundant of all elements. In the free state it forms about one-fifth, by volume, of the air. Chemically combined with hydrogen it forms eight-ninths, by weight, of water; united with other elements it constitutes about one-half the rocks in the earth's crust and over one-half of animal and vegetable matter.

20. Laboratory Preparation.—If mercuric oxide, HgO , is gently heated, it decomposes into the elements mercury

and oxygen. The mercury remains behind as a liquid and the oxygen passes off as a gas. This change or reaction may be produced in a simple way. If a small amount of mercuric oxide, which is a red powder, is heated in a test tube, Fig. 8, the sides of the tube become lined with a mirror of mercury which after a short time separates into little drops. If a match, previously lighted and extinguished, but still bearing a tiny spark at the end, is thrust into the mouth of the tube, it at once



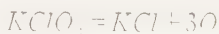
Fig. 8.

reignites and burns brightly. This is known as the spark test for oxygen and is well worth remembering, for it serves as a simple means of detecting oxygen.

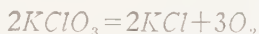
Priestly, in 1774, used this method to prepare what he called *dephlogisticated air*, which was in reality oxygen. This method of making oxygen, though of historical interest, is too expensive to be used as a regular means of preparation. The reaction is $2HgO = 2Hg + O_2$.

The most convenient method of preparing oxygen is to gently heat potassium chlorate, $KClO_3$, which readily breaks up

into potassium chloride, KCl , and oxygen. The course of the reaction may be represented by the equation,



But, according to the table of atomicities, in the preceding Section, oxygen is diatomic and the molecule must be written O_2 ; therefore, the correct equation would be



By inspection, it may readily be ascertained that there are the same number of atoms of each element on each side of the equality sign.

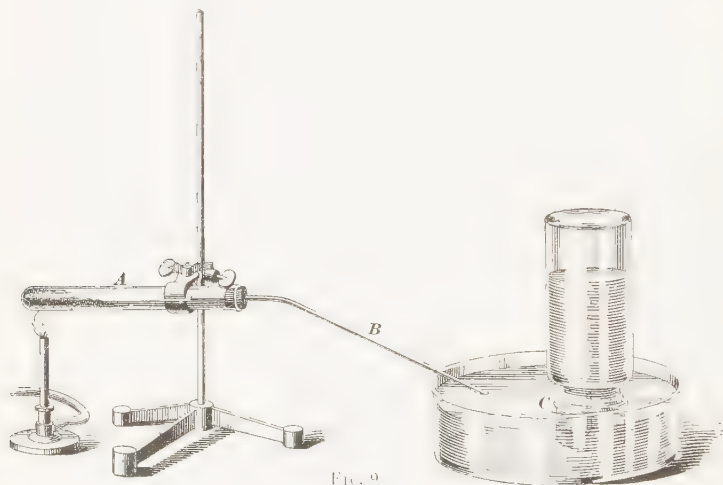
21. The preparation and collection of oxygen can be effected by using an arrangement such as is shown in Fig. 9. Sufficient potassium chlorate, a white solid, is placed in the test tube A to fill the bottom of the tube to the height of $\frac{1}{2}$ inch and heat is then gently applied. The substance crackles and the crystals split up. This explosive splitting up of crystals, when heated, is called *decrepitation*. The potassium chlorate gradually melts and appears to boil, at which point it breaks up easily, with the liberation of oxygen. The spark test, already described, may be used to prove the presence of oxygen.

It has been found that the presence of manganese dioxide, MnO_2 , causes potassium chlorate to decompose and liberate oxygen more readily, and at a lower temperature, than when it is absent. While potassium chlorate alone does not give off oxygen below $351^\circ C.$, the mixture of potassium chlorate and manganese dioxide gives it off readily at $200^\circ C.$

22. The manganese dioxide acts merely by its presence in some undetermined manner and is not itself affected; it may, therefore, also be called a catalytic agent. It has been determined, experimentally, that the highest yields of oxygen are obtained by using 1 part by weight of manganese dioxide with 3 parts by weight of potassium chlorate. Heating a mixture of potassium chlorate and manganese dioxide is usually resorted to when a small quantity of oxygen is needed in the laboratory and there is no other source of supply available.

23. Preparing and Collecting Oxygen.—The 6-inch tube *A*, Fig. 9, is filled about one-third full with the potassium chlorate-manganese dioxide mixture and a wire is pushed through the mixture to the bottom of the tube to make a passage for the oxygen evolved. The tube is then connected to a delivery tube *B*, by means of a tightly fitting stopper, and is adjusted so that the delivery tube extends into the trough to the side opening of the beehive shelf.

The collecting bottle, filled to the brim with water, is then put in position by placing the palm of the hand over the mouth of the bottle, inverting the bottle, placing the neck of it under



the surface of the water in the trough, without losing any of the water in the bottle, and then removing the hand. Care must be taken to keep the neck of the water-filled bottle under the surface of the water in the trough lest some of the water should escape from the bottle and be replaced by air.

The mixture in the test tube is gently warmed at the end near the stopper and the flame is brought slowly toward the other end of the tube as oxygen is evolved. This procedure prevents clogging of the delivery tube with loose dust carried over by the current of oxygen. The burner is withdrawn from the test tube when the bottle is two-thirds full of oxygen, and

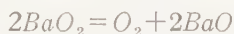
the end of the delivery tube is withdrawn from the water as soon as the bottle is full of oxygen; otherwise, the contraction of the gas, as it cools in the apparatus, would draw water into the test tube and cause it to crack. The bottle containing oxygen is placed with its mouth upwards, for oxygen is heavier than air, and is covered with a piece of glass to insure the retention of the gas in the bottle.

24. Commercial Preparation of Oxygen.—(Oxygen is obtained, commercially, from water and air, for these are the most abundant of all sources, and oxygen can be extracted from them in a practical and economical way.

Porous barium oxide, BaO , is used in one process to take oxygen from the air under one set of conditions and give it up under another. Originally, barium oxide was heated to a dull redness in a current of air, free from carbon dioxide, CO_2 , to form barium dioxide, BaO_2 , as follows:



The heat was raised to a bright redness so as to decompose the barium dioxide into oxygen, which was collected, and barium oxide, which was used over again. The reaction is as follows:



Owing to the fact that the barium oxide became non-porous and glassy after it had been used about ten times, and so was no longer able to take up oxygen, the process was too expensive to be worked on a commercial scale.

25. The Brin Process.—In this process the objectionable feature of the preceding process has been overcome. This method consists in heating barium oxide to a dull redness in retorts while forcing pure air in under a pressure of about 15 pounds per square inch. As soon as the barium oxide has been changed to barium dioxide the pressure pump is reversed and the air is exhausted from the retort to produce a vacuum. The temperature is not changed. Under these conditions, the barium dioxide breaks up into oxygen, which is collected, and porous barium oxide, which can be used continually for six

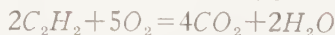
months before it needs to be renewed. This process is a commercial success.

The formation of barium dioxide from oxygen and barium oxide, and the decomposition of barium dioxide to form barium oxide and oxygen, form an excellent example of a *reversible* reaction.

26. Properties of Oxygen.—Oxygen is a colorless, tasteless, odorless, and invisible gas. It can be condensed to form a pale-blue liquid that boils at -182.9° C. It is slightly soluble in water, about 4 volumes dissolving in 100 volumes of the solvent, and is slightly heavier than air. It does not burn, but many other substances can burn in it. It is necessary for the breathing of men and animals, for without it they would suffocate.

Oxygen unites, chemically, with all elements, except fluorine, helium, and argon. It is one of the most active of all elements and, when pure, combines with other substances with great vigor. For example, finely powdered iron combines with an evolution of light and heat with pure oxygen, and warm phosphorus, placed in pure oxygen, unites much more rapidly with it than with oxygen in air. Glowing carbon, plunged into pure oxygen, burns with greater activity than in air. A small spark at the end of a match, placed in pure oxygen, reignites the match and causes it to burn. The oxygen of air is not as active, chemically, as pure oxygen, because it is weakened in its action by the presence of nitrogen, for the latter element does not combine chemically with any other element under ordinary conditions and merely serves to dilute and weaken the activity of the oxygen with which it is mixed.

27. Uses of Oxygen.—Pure oxygen is used chiefly with the gases hydrogen and acetylene to get high temperatures. The oxyhydrogen flame has already been described under Uses of Hydrogen. *Acetylene* has the formula C_2H_2 . The change that takes place when acetylene and oxygen unite is:



The oxyacetylene flame is used for practically the same purposes as the oxyhydrogen flame.

Oxygen is also used in first-aid work around mines, in the manufacture of oils, in the ageing of liquors, in the refinement of glass, and in medicinal pursuits.

The uses so far mentioned require the pure gas. The oxygen of the air is an indispensable agent in the generation of light and power from fuels. Without it, combustion of coal, wood, oils, and other fuels would be impossible. Atmospheric oxygen also combines with other elements in a wide variety of ways to help sustain life, for it serves as a means whereby the energy of living beings is stored up and then used. In all, it is an indispensable adjunct to the world, for without it living things could not exist.

OXIDATION AND REDUCTION

28. Oxidation.—The process in which oxygen unites with other substances is called **oxidation**. This action may be slow, as in the rusting of iron, or rapid, as in the burning of carbon. The product formed by the chemical combination of oxygen and any other element is called an **oxide**. For example, PbO is *lead oxide*, SnO is *stannous oxide*, K_2O is *potassium oxide*, and H_2O , commonly called water, is *hydrogen oxide*. This is but one small phase of the system of naming substances, which has already been described in another Section.

29. Oxidizing Agents.—An *oxidizing agent* may be defined as a substance that causes an element or compound to combine with oxygen or with other elements of similar character or that *increases its valence*. The following are common examples of oxidizing agents and their reactions:



In the first equation, metallic iron is oxidized to ferric oxide and in the second equation, ferrous chloride is oxidized to ferric chloride, the valence of iron being increased from 2 to 3 in each case. Oxygen and chlorine in these reactions are called oxidizing agents.

30. Combustion.—The term **combustion**, in its broad meaning, is applied to processes in which substances combine vigorously with an evolution of light and heat, though most commonly it is considered as an oxidizing process, because it is a vigorous combination of a substance with oxygen with the evolution of light and heat. This action is also called *burning*. The temperature below which a substance does not burn is called the **kindling point** of that substance. Each substance has its own kindling point. For example, wood may be exposed to the action of oxygen for years without burning. If, however, the temperature of the wood is raised to the kindling point, it at once ignites and burns vigorously with the evolution of light and heat.

If the burning substance is a gas, or if, on burning, it gives off a gas, the result is a *flame*. Carbon, when it burns, first forms the gas carbon monoxide, CO , which in turn unites with more oxygen to form carbon dioxide, CO_2 . The flame that appears when carbon burns is merely the burning of the carbon monoxide to carbon dioxide. Hence, a *flame* is a burning gas.

31. Reduction.—The action opposite in its effects to that of oxidation is termed a reduction, and is defined as the process in which oxygen is taken from substances. For example, when hydrogen and cupric oxide react chemically, the hydrogen takes oxygen from the cupric oxide to form copper and hydrogen oxide (water); thus,



Hydrogen acts as a *reducing agent* in this change, because it takes oxygen from cupric oxide; that is, it reduces cupric oxide to copper. Cupric oxide can, in this case, be considered an *oxidizing agent*, for it oxidizes hydrogen to hydrogen oxide, or water.

32. Reducing Agents.—The native compounds or ores, from which metals are derived, are in many cases oxides or sulphides of such metals. The process used to obtain these metals in a free or uncombined state is known as the reduction of the ore to its metallic state. From this a **reducing agent**

may be defined as a substance that removes oxygen, or elements similar to it, from compounds, or that decreases the valence of an element, changing it from a higher to a lower state of oxidation.

Owing to the avidity with which hydrogen combines with oxygen, it is one of the most prominent and powerful reducing agents. Thus, if hydrogen is passed over red-hot iron oxide, the metal is obtained in the free state, according to the following equation:



The following equation illustrates what is meant by a decrease in valence:



In this reaction ferric chloride is reduced to ferrous chloride by means of stannous chloride, which in turn is oxidized to stannic chloride.

OZONE

Allotropic oxygen. Formula O_3 . Molecular weight 48

33. Occurrence.—Van Marum, in 1785, first noticed that a peculiar, fresh, penetrating odor was given off around electrical machines in operation, but it was not until 1840 that the source of this odor was definitely determined. In that year, Schönbein proved that it was due to the formation of a gas containing three atoms of oxygen to the molecule. In other words, he found it to be oxidized oxygen having the formula O_3 graphically written as $\begin{array}{c} O \\ \diagup \quad \diagdown \\ O \quad -O \end{array}$, and now known as

ozone. Thus, oxygen is found to exist in molecular form as two distinct substances, ordinary oxygen and ozone. When two or more forms result from the same element, as, for example, oxygen and ozone from the element oxygen, such forms are said to be *allotropic*. Ozone is an allotropic modification of oxygen.

Ozone occurs in nature only where there is a natural or an artificial production of electricity.

34. Preparation.—While ozone can be prepared in several ways, the only method of any practical value is the one that depends on the passage of a current of electricity through air or oxygen. The laboratory and the commercial methods differ from each other only in the size of the equipment and the quantities made. All ozone generators, though differing in mechanical details, depend on the principle that ozone is formed when electrical discharges are passed through air, in which case the oxygen atoms rearrange themselves, as shown in the following equation:



The satisfactory technical production of ozone from air depends largely on the condition of the air, the best results being obtained when a dry, dense, cold air is used. The most successful plants are, therefore, those that have a process of refrigeration for the pre-treatment of air. Cooling to 0° C. gives excellent results, further cooling being unnecessary, for the maximum amount of ozone obtained from oxygen in air, 7.5 per cent., is obtained at 0° C.

35. Properties of Ozone.—Ozone is a colorless gas that becomes blue when subjected to pressure. Liquefied, it is deep blue, highly magnetic, and boils at -119° C. Ozone has a penetrating odor, not unlike that of chlorine. It is more soluble in water than oxygen, for at 12° C. 50 volumes of ozone are dissolved in 100 volumes of water.

It decomposes in the presence of oxidizable substances, particularly organic matter, and is stable only when mixed with oxygen. Heated to 250° C., it decomposes to form oxygen; thus,



It is obvious from the change of oxygen to ozone and that from ozone to oxygen that some reactions can be reversed by changing the conditions under which the reacting substances exist. By passing electric charges through air, ozone can be formed; by heating ozone sufficiently high, oxygen can be produced. These changes can be reversed by altering the conditions under which the reacting substances exist and are

reversible actions. The changes can, therefore, be written thus,



These changes clearly show that the reactions which chemicals undergo are dependent on conditions, such as temperature, concentration, pressure, and many other circumstances.

36. Ozone is a much more active oxidizing agent than oxygen, for the first stage in its decomposition results in the liberation of nascent oxygen, in which condition it is especially active. In the presence of many substances, this nascent oxygen atom can combine to form new substances. For example, ozone can remove the color from organic dyes by oxidizing them. It can, by direct combination, form oxides with metals, such as mercury and silver; thus:



Ozone acts on potassium iodide in the presence of water to form new substances. If starch is present during this change, a deep-blue color results. The following equation shows the change that takes place:



That is, 1 molecule of ozone reacts with 2 of potassium iodide and 1 of water to form 1 molecule of oxygen, 2 of potassium hydroxide, and 1 of iodine. *Schönbein's test* for ozone is based on this chemical change and is carried out by dipping a piece of filter paper into a starch emulsion containing a little potassium iodide, and then introducing the paper into the gas being tested. If ozone is present, a deep-blue color will appear. This blue color is due to iodo-starch, which is a solution of iodine in the solid starch that is suspended in water.

It should be borne in mind that, while the gases oxygen and ozone are both made up of atoms of the same element, they are different substances, having different molecular weights, densities, and degrees of chemical activity and stability.

37. Uses for Ozone.—The commercial value of ozone depends on the fact that it can oxidize substances at a very low temperature; much lower than that at which oxygen does.

Ozone readily oxidizes organic matter. For example, it can destroy the organic odors that result from human and indus-

trial activities and can change the nature of the disagreeable odors that prevail in meeting places, schools, glue factories, slaughter houses, chemical works, fertilizer plants, and many other establishments where disagreeable odors are generated. Ozone is, therefore, a valuable adjunct to ventilation systems.

Probably the most important of all uses for ozone is in the purification of water. Ozone, mixed with water by means of various mechanical devices, destroys the odor, unpleasant taste, and undesirable color of waters by oxidizing the organic bodies that cause these objectionable properties. It also destroys the bacteria present. The gas is especially valuable for purification of water, because it is non-poisonous, leaves no taste, and is not absorbed by the water to any appreciable extent.

The industrial uses of ozone are constantly being increased. Tallows, fats, and oils can be made tasteless and odorless, and can be bleached and purified by the action of ozone. It is often found preferable to chlorine, as a bleaching agent for various fabrics, because it is neither poisonous nor as objectionable to workmen as chlorine. It is used to some extent to convert linseed oil into varnish, and finds some application in the brewing industry to purify casks and water.

OXIDES OF HYDROGEN

WATER, OR HYDROGEN MONOXIDE

Formula H_2O . Molecular weight 18.016. Specific gravity (water at 4° C.) 1.00. Boiling point (water) 100° C. Freezing point (water) 0° C.

38. Occurrence.—Hydrogen monoxide, or water, occurs in nature as ice, water, and steam. It is commonly observed in the forms of springs, wells, rainfall, lakes, rivers, seas, and oceans; constitutes a large part of all living bodies, and is found to some extent in minerals. It is the most abundant of all compounds and occurs in every part of the world.

Water, the liquid form in which condition hydrogen monoxide is most commonly found, seldom occurs in the pure state,

for it constantly dissolves and mechanically carries many of the substances with which it comes into contact. Sea-water, for example, holds over 3.5 per cent. of solid matter in solution, and even rainwater, the purest of all natural waters, contains a part of the atmospheric gases with which it comes in contact.

Water can be made suitable for laboratory use by distilling it, as described in a previous Section. The treatment of water for industrial purposes varies with the nature of the water and the use to which it is to be put, for an impurity may be harmless for one purpose and objectionable for another.

39. Effect of Heat on Water.—The chemist should be familiar with the various properties of water, for they are constantly being used to produce all kinds of effects in chemical operations. This is especially true of the action of heat on hydrogen monoxide, for power generation in steam plants depends on the influence of temperature on the substance.

Below 0° C. water exists as a solid, called *ice*. Suppose that the temperature of the ice is -5° C., and that heat is applied. As the temperature of the ice rises, the mass expands, that is, increases in volume. When the temperature of the ice reaches 0° C., it begins to melt. It has been found that the temperature remains at 0° C. during the melting process and does not rise again until every particle of ice has been changed to water. The volume of the water is less than that of the ice, and continues to diminish until 4° C. is reached. From this temperature the volume of the water expands until 100° C. is reached. The temperature 4° C., from which point changes in temperature cause the mass of water to expand, is the temperature at which water has its maximum density; that is, the point at which it weighs most per unit volume. A cubic centimeter of water at 4° C., for example, weighs 1 gramme, and is heavier than a cubic centimeter of water at any other temperature.

As the water is heated, its temperature increases until 100° C. is reached. At this point it commences to boil and does not change in temperature until all the water has been changed to steam at 100° C.

40. Physical Properties of Water.—No substance is used more by chemists and pharmacists than water. To know its properties is to know the properties of most liquids, for they follow the same general principles and differ from one another only in details. Great attention should therefore be given to the study of water, for familiarity with this material does much to broaden one's point of view in chemistry.

Water has neither taste nor odor. A layer of pure water of sufficient thickness has a greenish-blue tint, even though thin layers exhibit no color. Often the impurities, always present in natural waters, impart odor, taste, and color to the liquid.

41. Chemical Properties of Water.—Water is not easily decomposed by heat, even at high temperatures. Substances, such as water, that are not easily decomposed are said to be *stable*. Water can combine with oxides to form new substances.

When water acts on calcium oxide, commonly called *quicklime*, there is formed a new substance, calcium hydroxide, $\text{Ca}(\text{OH})_2$, sometimes called *slaked lime*. Following is the reaction that takes place:



Water can also combine with many oxides, other than calcium oxide, to form various hydroxides. It can unite, for example, with sulphur trioxide to form sulphuric acid; thus:



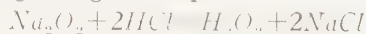
HYDROGEN DIOXIDE, OR HYDROGEN PEROXIDE

Formula H_2O_2 . *Molecular weight* 34.016

42. Occurrence.—Hydrogen dioxide, also called hydrogen peroxide, is not ordinarily found in nature, though minute quantities have at times been detected in rain and snow. Artificial means must be resorted to to get the substance in usable amounts.

43. Laboratory Preparation.—Hydrogen dioxide can be made on a small scale by adding sodium peroxide, Na_2O_2 , a

little at a time, to a weak solution of hydrochloric acid, in which case the following change takes place:



The mixture of hydrogen peroxide, sodium chloride, and water (water is introduced in the hydrochloric-acid solution and takes no direct part in the chemical change) is thoroughly and repeatedly shaken with ether. Upon standing, the mixture separates into layers, the solution of hydrogen peroxide and water, in ether, rising to the top and the salt and part of the water settling to the bottom. The ethereal solution of water and hydrogen peroxide, after being drawn off, is distilled at a low temperature (about 45° C.) to evaporate the ether from the mixture, thereby leaving an aqueous solution of hydrogen peroxide.

Hydrogen dioxide can also be made by shaking crystalline barium dioxide, $BaO_2 \cdot 8H_2O$, in a weak solution of cold sulphuric acid, during which operation the following reaction takes place:



NOTE.—The formula $BaO_2 \cdot 8H_2O$ could also be written as follows: $BaO_2 + 8H_2O$, but it would fail to show that the eight molecules of water represent water of crystallization, chemically combined with the barium dioxide. In such cases the plus sign is replaced by a period, as shown.

Pure hydrogen peroxide is separated from the barium sulphate and water present by distilling the mixture *in vacuo*; that is, under reduced pressure. Water boils at a lower temperature than hydrogen peroxide; in fact, the latter decomposes with violence into hydrogen monoxide and oxygen at 100° C., the boiling point of water. Therefore, to distil a mixture of hydrogen peroxide and water with safety, one must keep the temperature below 100° C. Hydrogen peroxide can be vaporized at temperatures ranging from 45° C. to 85° C., when the pressure exerted upon it is reduced to about 68 millimeters. The distillate that passes over first, consisting mostly of water, is discarded, and the latter part, consisting mainly of hydrogen peroxide, is collected.

44. Technical Production of Hydrogen Peroxide. Hydrogen peroxide is made on a commercial scale by decom-

posing barium dioxide with sulphuric acid or phosphoric acid, H_3PO_4 . A mixture of barium dioxide and water, about the thickness of cream, is prepared and then added slowly to the cold acid, the temperature being kept below 15° C. After the proper amount, determined by experience, has been added, the precipitate of barium sulphate or barium phosphate, depending on whether sulphuric acid or phosphoric acid has been used, is allowed to settle. The clear liquid, containing hydrogen peroxide and a little excess of acid, is then poured off. The slight excess of acid is allowed to remain in the solution of hydrogen peroxide, because it has been found that the substance is more stable in an acid than in an alkaline or in a neutral (neither alkaline nor acid) solution. The mixture of water and hydrogen peroxide can be further separated by distilling *in vacuo*, as previously described. Phosphoric acid is often given the preference over sulphuric acid in the foregoing process, because it precipitates impurities, such as iron and manganese, contained in the barium dioxide, and thereby produces a purer product than does sulphuric acid, which chemical does not remove these impurities.

Hydrogen peroxide can also be manufactured by the action of hydrofluoric acid on barium dioxide in lead-lined tanks. The tanks are lead lined to prevent chemical action between hydrofluoric acid and the metal, usually, iron, from which the tanks are made, for lead is not readily acted on by hydrofluoric acid. The mixture of the acid and the dioxide is stirred continuously and kept at as low a temperature as possible, for it has been found that best results are obtained under these conditions. The reaction, which is complete in about 12 hours, is shown by the equation:



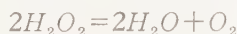
The clear liquid is drawn off after the insoluble barium fluoride has settled. The barium fluoride is treated with sulphuric acid to recover hydrofluoric acid, which product can be used again. The following reaction takes place during this recovery operation:



The insoluble barium sulphate is separated from the hydrofluoric acid by decantation.

45. Properties of Hydrogen Peroxide.—Pure hydrogen peroxide is a syrupy liquid having a specific gravity of about 1.5. It can be cooled to a solid that melts at -2°C ., and can be boiled at 85°C ., when the pressure exerted upon it is reduced to 68 millimeters. It is soluble in all proportions in both water and alcohol.

Hydrogen peroxide is chemically active, for it gives up 1 atom of oxygen from each molecule present, at a temperature even as low as -20°C . It is fairly stable in dilute aqueous solutions, especially when small amounts of free acid are present. Alkalies and salts have a tendency to hasten the decomposition of the substance. It has been found that the addition of preservatives tends to prevent the decomposition of hydrogen peroxide. For example, the organic substance acetanilide is used in commercial peroxide, for even as small an amount as one-half of 1 per cent. will increase the stability of the solution to such an extent that less than 3 per cent. will decompose in half a year. Light also has a tendency to hasten the decomposition of hydrogen peroxide. For this reason, the commercial product is generally sold in dark-colored bottles. Finely divided metals, such as silver and platinum, cause the substance to decompose rapidly. These metals act by their mere presence and take no direct part in the reaction, as shown in the equation:



In solution, hydrogen peroxide acts as a feeble acid, for it turns blue litmus red and reacts with some substances in a manner similar to that of acids; thus:

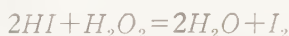


Strontium hydroxide reacts with hydrogen peroxide to replace the hydrogen atoms in hydrogen peroxide with strontium. An acid, like sulphuric acid, will react in a like manner, as shown in the equation:



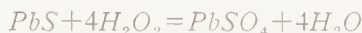
In this instance, the strontium replaces the hydrogen atoms in the sulphuric acid.

46. The most prominent chemical characteristic of hydrogen peroxide is its power to supply oxygen readily; that is, its power as an *oxidizing agent*. It is even more active than oxygen, O_2 , in this respect, for it liberates oxygen in the nascent state, O , as shown in the equation $H_2O_2 = H_2O + O$, in which condition it is very active. It can liberate iodine from hydrogen iodide; thus:



Two molecules of hydrogen iodide react with 1 molecule of hydrogen peroxide to produce 2 molecules of hydrogen monoxide, or water, and 1 molecule of iodine.

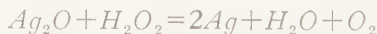
Hydrogen peroxide can convert sulphides into sulphates, as shown in the equation:



One molecule of lead sulphide is oxidized by 4 molecules of hydrogen peroxide into 1 molecule of lead sulphate; 4 molecules of hydrogen monoxide, or water, are also produced.

It is an excellent oxidizing agent for many organic compounds. In the case of dyes, it oxidizes them, changes their chemical nature, and, therefore, destroys their color. A dye retains its color only as long as its chemical composition remains unaffected.

Hydrogen peroxide can, under certain conditions, act as a *reducing agent*; that is, as an agency for the removal of oxygen from a compound. Thus, silver oxide is reduced by hydrogen peroxide to silver:



(See also the United States Pharmacopœia, 9th Revision, page 246.)

47. Uses of Hydrogen Peroxide.—Substances that react chemically with coloring matter to form either colorless or lighter-hued products are called *bleaching agents*. Hydrogen peroxide, owing to its power to oxidize organic coloring matter to lighter-colored substances, is used as a bleaching

agent and is applied to delicate materials, such as straw, feathers, hair, ivory, and silk, that are liable to be damaged by stronger bleaches. A mixture of sodium peroxide, acid, and water, which substances react to produce hydrogen peroxide, as has already been explained, is often used for this purpose under the name *soda bleach*.

Blackened paintings, containing lead colors, are often restored to their original tints by hydrogen peroxide. The black color is due to lead sulphide formed by the action of hydrogen sulphide, often found in the air of cities, on the lead compounds in the painting. Hydrogen peroxide oxidizes the black lead sulphide to the light-hued lead sulphate.

Hydrogen peroxide is used very largely in surgical, medicinal, and hygienic work, for it readily liberates nascent oxygen, an agent that kills bacteria, prevents infection, and improves hygienic conditions. It probably prevents infection by destroying the organisms causing tissue decomposition and by oxidizing the intermediate products of decomposition.

Hydrogen peroxide is sold in solutions of various strengths, the most common of which are 3 per cent. and 30 per cent. The strength of a hydrogen peroxide solution is also expressed in terms of the volume of oxygen liberated from a unit volume of solution. For example, a solution marked *10 volumes* can liberate 10 cubic centimeters of oxygen gas from 1 cubic centimeter of solution. A 3 per cent. solution evolves about 10 volumes of oxygen from every volume of solution.

NOTE.—All references to the United States Pharmacopœia are to the 9th Revision, and will be indicated by the letters U. S. P.

NITROGEN

PROPERTIES, PREPARATION, AND COMBINATIONS

Symbol N. Atomic weight 14.008. Molecular weight 28.016. Valence I to V.

48. History.—Nitrogen was discovered in 1772, by Ruth-erford, a professor of botany in the University of Edinburgh,

who showed that air, after it had been breathed by an animal, and washed with lime water, contained a gas that would support neither respiration nor combustion. Scheele and Lavoisier soon afterwards found, independently of each other, that this substance constituted four-fifths of the air, by volume. Lavoisier recognized it to be an element and called it *azote*, because it did not support life. The English name indicates that it is a constituent of saltpeter, KNO_3 , the Latin name for which is *nitrum*.

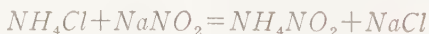
49. Occurrence.—As already stated, air consists of approximately four-fifths of nitrogen, but aside from this source, nitrogen is found in many forms of combination with oxygen and metals, such as potassium and sodium. Chile saltpeter is sodium nitrate. Nitrogen is also an essential constituent of many vegetable and animal substances.

50. Preparation.—Nitrogen, containing a small amount of argon, may be obtained from pure air by the removal of the oxygen from the latter by passing air over heated copper. Commercially, nitrogen is obtained by the evaporation of liquid air.

The easiest method of preparing pure nitrogen is to heat ammonium nitrite. The reaction goes as follows:



Ammonium nitrite, however, is a very unstable compound and cannot be easily kept, so, in practice, a strong solution of ammonium chloride, NH_4Cl , and sodium nitrite, $NaNO_2$, are mixed, the reaction taking place as follows:



and when heat is applied, the ammonium nitrite breaks up, setting nitrogen free.

Nitrogen may also be prepared by passing air through a red-hot tube containing copper or iron filings.

51. Physical Properties.—Nitrogen is a colorless, odorless, and tasteless gas; it is lighter than air, and has a specific gravity of .967. It extinguishes burning bodies and is not itself combustible. Nitrogen has been liquefied at temperatures

below -146° C. at a pressure of 35 atmospheres; at atmospheric pressure, the liquid boils at -195.5° C. The gas is soluble to the extent of 1.6 volumes in 100 volumes of water.

52. Chemical Properties.—Nitrogen, in a free state, is a remarkably inert body, combining directly with only a very small number of elements. At ordinary temperatures it is almost absolutely indifferent. However, passed through a tube over strongly heated calcium, magnesium, or lithium, the nitrides of these elements are formed. They have the formulas, Ca_3N_2 , Mg_3N_2 , and Li_3N , respectively. Nitrogen combines with difficulty with hydrogen to form ammonia, and with still greater difficulty with oxygen to form nitric oxide, NO ; but, although the gas is very inert, the compounds that it does form are among the most energetic known.

COMPOUNDS OF NITROGEN WITH HYDROGEN

AMMONIA

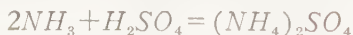
Formula NH_3 . *Molecular weight* 17.032

53. History.—Gaseous ammonia was discovered by Priestly, in 1774, when he collected the gas evolved by the action of lime on sal ammoniac, NH_4Cl . Priestly named the gas *alkaline air*. An ammoniacal liquid, called *spirits of harts-horn*, was also obtained by the destructive distillation of the hoofs and horns of animals.

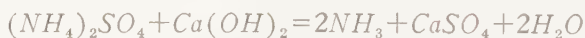
54. Occurrence.—Ammonia exists, in the free state, in small quantities in the air and in rainwater. It is generally a post-mortem product, as dead animal and vegetable matter yields it in putrefaction. The urine and excrement of animals contain refuse nitrogenous matter that, on being exposed to the air, is changed into ammonia and in this way causes these substances to be such valuable fertilizers, as most plants are incapable of assimilating nitrogen in a free state but are able to do so when that element is presented to them as ammonia.

The compounds of ammonia are found in beds of *guano* (the excrement of sea fowl) on certain ocean islands. The most important of these compounds, *ammonium chloride*, also called *sal ammoniac*, was first obtained from Egypt. The name ammonia is said to be derived from that of Jupiter Ammon, owing to the circumstance that near a temple dedicated to this god the Arabs extracted one of the compounds of ammonium from the dung of camels. Quills, horn, hair, etc. heated in a closed vessel evolve a number of gases, among which ammonia is always present. Coal (fossilized plants) contain about 2 per cent. of nitrogen, and in its destructive distillation for the manufacture of gas, ammonium compounds are always obtained.

55. Preparation.—An industrial method for the production of ammonia results from the manufacture of coke and illuminating gas. In this process, the gases that are given off during the dry distillation of coal are passed through water, which dissolves out the ammonia. The ammonia liquor is then heated with milk of lime, $Ca(OH)_2$, and the escaping ammonia is led into concentrated sulphuric acid. In this way crystallized ammonium sulphate is obtained. Thus,



After recrystallization the ammonium sulphate is again distilled with milk of lime, and the ammonia set free is recovered.



In the laboratory, ammonia may be prepared by heating an ammoniacal salt, such as ammonium chloride, with a stronger base. For instance, if ammonium chloride, NH_4Cl , and slaked lime, $Ca(OH)_2$, are heated together, the following reaction occurs:

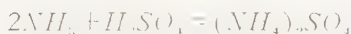


In order to completely decompose the ammonium chloride, about 2 parts lime are used to 1 part ammonium chloride.

56. Physical Properties of Ammonia.—Ammonia, at ordinary temperatures, is a gas with a characteristic odor, being

poisonous when breathed in large quantities. It has a density of 8.5, and a specific gravity of .589 (air=1). One liter of the gas at 0° C. and at a pressure of 760 millimeters weighs .7708 gramme. The gas can be easily liquefied; it boils at -33.7° C., and becomes solid at -75° C. It is extremely soluble in water; at 0° C. and at normal pressure, 1 volume of water dissolves 1,148 volumes of ammonia or .875 parts by weight. The evaporation of liquid ammonia causes a considerable depression of temperature. This is the principle on which most of the ice machines now in use are based.

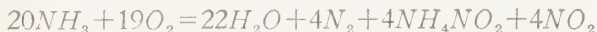
57. Chemical Properties.—The characteristic property of ammonia is that it combines directly with acids to form salts. Thus,



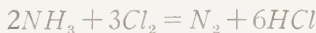
In these salts, the group NH_4 acts as a metal. The group, or radical, NH_4 is called *ammonium*; so far, it has resisted all attempts to isolate it.

The reactions described under (a), (b), (c), and (d) should be noted.

(a) Ammonia does not burn in air, but does so in oxygen, water, and nitrogen, traces of ammonium nitrite, NH_4NO_2 , and nitrogen dioxide, NO_2 , being formed. A mixture of ammonia and oxygen explodes violently when ignited. Or,



(b) Chlorine takes fire when passed into ammonia, nitrogen, and hydrochloric acid, HCl , being formed.

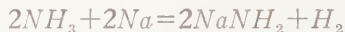


The latter unites with the remaining ammonia to form ammonium chloride, commonly called *sal ammoniac*.

(c) The hydrogen of ammonia is replaceable by metals. Magnesium burns in ammonia, forming magnesium nitride, Mg_3N_2 . Or,



(*d*) When ammonia is conducted over hot sodium or potassium, sodium amide, NaNH_2 , or potassium amide, KNH_2 , is formed, respectively. Or,



(See also, U. S. P., pages 43, 44, 45, 53, 207, 232, 404, and 522.)

COMPOUNDS OF NITROGEN WITH CHLORINE AND IODINE

NITROGEN CHLORIDE AND NITROGEN IODIDE

58. Nitrogen Chloride.—When chlorine gas is passed into a warm concentrated solution of ammonium chloride, nitrogen chloride, or, more properly, nitrogen trichloride, NCl_3 , separates as a heavy liquid. It is a very dangerous explosive.

59. Nitrogen Iodide.—Nitrogen iodide, $\text{N}_2\text{H}_3\text{I}_3$, is formed when an alcoholic solution of iodine is added to a solution of ammonium hydroxide. It is also a violent explosive.

OXIDES AND ACIDS OF NITROGEN

60. Classification.—There are five oxides, three oxygen acids, and three sodium salts of these acids. They may be classified as shown in Table II.

TABLE II
OXIDES, ACIDS, AND SALTS OF NITROGEN

Oxides		Acids		Salts	
Name	Formula	Name	Formula	Name	Formula
Nitrous oxide	N_2O	Hyponitrous acid	$\text{H}_2\text{N}_2\text{O}_2$	Sodium hyponitrite	$\text{Na}_2\text{N}_2\text{O}_2$
Nitric oxide	NO				
Nitrogen trioxide . .	N_2O_3	Nitrous acid	HNO_2	Sodium nitrite	NaNO_2
Nitrogen peroxide . .	NO_2				
Nitrogen pentoxide .	N_2O_5	Nitric acid	HNO_3	Sodium nitrate	NaNO_3

NITROUS OXIDE

Formula N_2O . *Molecular weight* 44.016

61. Preparation.—Nitrous oxide may be prepared by carefully heating ammonium nitrate, NH_4NO_3 , to about $250^\circ C$. Or, $NH_4NO_3 + \text{heat} = N_2O + 2H_2O$

62. Properties.—Nitrous oxide is a colorless gas with a faint, sweetish odor and a distinctly sweet taste. It may be condensed to a liquid by a pressure of 32 atmospheres at $0^\circ C$., or at ordinary pressure at $-88^\circ C$. The liquid freezes also by its own evaporation, when allowed to escape into the open air, producing a snowlike mass. Nitrous oxide supports combustion nearly as vigorously as oxygen; a wax taper having a spark on its wick is relighted in it, as in oxygen. Phosphorus, as well as sulphur, burns in it with great splendor, the gas being decomposed and its oxygen uniting with the combustible, forming oxides, while the nitrogen is liberated. It is quite soluble in cold water, but only very sparingly in warm water; 100 parts of water at $15^\circ C$. dissolve nearly 78 parts of the gas. It is still more soluble in alcohol and alkaline solutions.

Nitrous oxide acts as an anesthetic, when inhaled (that is, it is a substance that causes insensibility to pain). It was with this gas that the effects of anesthesia were discovered by Wells, a discovery everywhere acknowledged as the crowning surgical discovery of the 19th century. About 4 or 5 gallons of the gas is sufficient in most cases to produce total insensibility; before this stage is reached, it induces a state of intoxication, often accompanied by violent fits of laughter, owing to which influence it has received the popular name of *laughing gas*. (U. S. P., page 280.)

HYPONITROUS ACID

Formula $H_2N_2O_2$. *Molecular weight* 62.032

63. Preparation.—Hyponitrous acid is formed when nitrogen trioxide is passed into a solution of hydroxylamine in methyl alcohol (CH_3OH). Thus,



It is a very weak acid. Upon the addition of the acid to a water solution of silver nitrate, insoluble *silver hyponitrite*, $Ag_2N_2O_2$, is precipitated. When this salt is shaken with an ethereal solution of HCl , hyponitrous acid is liberated and the resulting insoluble silver chloride may be separated by filtration. By evaporation of the ethereal solution, hyponitrous acid is obtained as a white crystalline solid which explodes when heated.

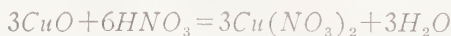
NITRIC OXIDE

Formula NO. Molecular weight 30.008

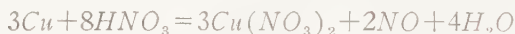
64. Preparation.—Nitric oxide may be prepared by allowing copper to act on dilute nitric acid. The nitric acid first oxidizes the copper, as is shown by the equation,



The copper oxide formed is at once dissolved by the excess of nitric acid, according to the equation:



Or, the two reactions may be stated in one equation; thus,



65. Properties.—Nitric oxide is a colorless gas, which, on coming in contact with the air, combines with the oxygen and forms higher nitrogen compounds of a ruddy tint. The strong odor noticed during its preparation is that of these higher oxides, and not that of the nitric oxide. It has almost the same specific gravity as air, namely, 1.039. It is more difficult to liquefy than nitrous oxide, its critical temperature being -93.5° C. at 71.2 atmospheres, and its freezing point -153° C.; when it solidifies it resembles snow. It is much more stable than nitrous oxide, and may be subjected to even a red heat without suffering decomposition. In consequence of this property, it does not accelerate combustion; a lighted taper plunged into a jar filled with it is immediately extinguished.

NITROGEN TRIOXIDE AND NITROUS ACID

Formulas N_2O_3 *and* HNO_2 . *Molecular weight of the oxide* 76.016, *of the acid* 47.016.

66. Composition and Preparation.—Nitrogen trioxide is also called *nitrous anhydride*, since two molecules of nitrous acid are formed upon the addition of water. Or,



Nitrogen trioxide may be prepared by the reduction of nitric acid by arsenious oxide:



By passing the evolved vapors through a freezing mixture, the nitrogen trioxide condenses to a rather unstable, greenish-blue liquid that reacts with water, producing *nitrous acid*.

67. Nitrous acid is a blue liquid, rather unstable at ordinary temperatures, but it may be preserved at a low temperature unaltered. At ordinary temperatures it is readily decomposed into nitric acid, water, and nitric oxide; thus,



The salts of nitrous acid are known as *nitrites*, and are stable.

NITROGEN PEROXIDE

Formula NO_2 *or* N_2O_4

68. Preparation.—Nitrogen peroxide may be prepared by mixing 2 volumes of nitric oxide with 1 volume of oxygen, when they combine according to the equation:



It is generally prepared by heating perfectly dry lead nitrate, which decomposes thus:



On passing the gases evolved through a freezing mixture, the peroxide is condensed to a liquid, and the oxygen escapes. If perfectly dry, the peroxide congeals to a white crystalline

solid at about -9° C. At 0° C. the liquid has a faint yellow color that gradually grows darker as the temperature is increased until it is a deep orange at about 24° C., at which point the liquid boils, evolving an orange vapor.

NITROGEN PENTOXIDE

Formula N_2O_5 . *Molecular weight* 108.016

69. Preparation.—Nitrogen pentoxide, which was first prepared by Deville in 1849, may be prepared by treating nitric acid with phosphorus pentoxide, a substance that has a strong affinity for water, when the following reaction takes place:



It is more readily obtained by passing chlorine over silver nitrate and condensing the product. The reaction is:



70. Properties.—Nitrogen pentoxide is a colorless, transparent solid. It melts at 30° C. and boils at 47° . It is very unstable, sometimes exploding spontaneously. It reacts energetically with water, producing nitric acid, according to the equation:

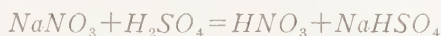


NITRIC ACID

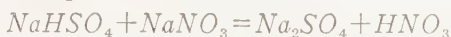
Formula HNO_3 . *Molecular weight* 63.016

71. Sources.—The salts of nitric acid, sodium and potassium nitrates, are the common sources of the acid. Potassium nitrate is found in India, Persia, and other oriental countries; it is called *Bengal saltpeter*. Sodium nitrate is found in Chile and Peru; it is called *Chile saltpeter*, or *caliche*. The deposit is about 5 feet thick, 2 miles wide, 220 miles long, and contains from 20 to 60 per cent. of sodium nitrate. Sodium and potassium nitrates are produced by the oxidation of nitrogenous organic matter in the presence of potassium or sodium.

72. Preparation.—Nitric acid is produced by the distillation of a nitrate—generally sodium or potassium nitrate—with sulphuric acid. The two are mixed in a retort, and on the application of heat, nitric acid, being volatile, distils over, leaving acid sodium sulphate. The reaction may thus be represented:



If two molecules of sodium nitrate are used to one of sulphuric acid and the temperature is increased, the resulting acid sulphate is decomposed as follows:



The temperature required for this reaction frequently decomposes a part of the nitric acid formed.

73. Properties of Nitric Acid.—Pure nitric acid is an unstable compound; at ordinary temperatures it is decomposed, to a slight extent by sunlight, turning yellow because of the small amount of nitrogen dioxide formed. At higher temperatures the acid breaks up, decomposing into nitrogen dioxide, water, and oxygen, the decomposition being complete at 260° C.

The 100 per cent. acid may be prepared by distilling the nearly pure acid of commerce with sulphuric acid under diminished pressure.

Nitric acid, when pure, is a colorless, fuming, corrosive, and strongly acid liquid, but usually has a faint yellow tinge, owing to the presence of some of the lower oxides of nitrogen, produced by its partial decomposition. Cooled to -47° C., the acid freezes, and heated to 86° C., it boils, undergoing partial decomposition. It is also readily decomposed by light. Chemically, it is a powerful oxidizing agent, acting on most of the metals with great vigor; gold and platinum, however, are not affected by it. Nitrogenous animal substances, such as parchment, silk, horn, and wool, are colored yellow by it, while any non-nitrogenous vegetable substances, such as cotton, sugar, glycerine, etc., are converted into violently explosive bodies.

74. The commercial nitric acid—sometimes sold under the name of *aqua fortis*—is of two sorts, called *single* and *double*.

Double aqua fortis is the ordinary concentrated acid of commerce, has a specific gravity of 1.42, and contains about 67 per cent. of $HN\text{O}_3$; the **single aqua fortis** has a specific gravity of 1.29, and contains about 46 per cent. of the pure acid.

Nitric acid, being a monobasic acid, can form only normal salts, which may be represented by the formula $M(NO_3)$, M standing for any monad metal. When free, nitric acid reddens litmus, bleaches indigo solutions, and evolves red fumes on introducing a little copper. Nearly all the non-metallic elements, sulphur, phosphorus, carbon, etc., are oxidized to their acids by it. The reactions of free nitric acid are also obtained from nitrates after treatment with sulphuric acid.

75. Uses.—Nitric acid finds wide use in the arts. It is employed for etching on metals, for oxidizing various substances, for forming certain substitution products, such as nitrobenzol and picric acid, and for the preparation of explosives, such as guncotton, nitroglycerine, etc. As all the metals in common use, except gold, platinum, and aluminum, are attacked by it, this acid is employed to distinguish and separate the first two metals from others of less value. The ordinary method of ascertaining whether a trinket is made of gold consists in touching it with a glass stopper wetted with nitric acid, which leaves gold untouched, but colors base alloys blue, from the formation of copper nitrate. The *touchstone* allows this method of testing to be applied with great accuracy. It consists of a species of black basalt, obtained chiefly from Silesia. If a piece of gold is drawn across its surface, a golden streak is left, which is not affected by moistening with nitric acid; while the streak left by brass, or any similar base alloy, is readily dissolved by the acid. Experience enables an operator to determine, by means of the touchstone, pretty nearly the amount of gold present in an alloy, comparison being made with the streaks left by gold alloys of known composition. (See also U. S. P., pages 18, 540, and 624.)

76. Aqua Regia, or Nitrohydrochloric Acid.—Neither nitric acid nor hydrochloric acid alone has the property of dissolving gold; but a mixture of 1 volume of nitric and 3 vol-

umes of hydrochloric acid, to which the name **aqua regia** has been given, readily dissolves gold. This property of dissolving gold depends on the presence of free chlorine, which is liberated by the action of the acids on each other, as shown in the equation:

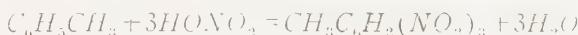


(Additional information is found in U. S. P., pages 18 and 19.)

77. Commercial Uses for Nitric Acid.—Nitric acid reacts with many organic compounds, such as phenol or carbolic acid, toluene, glycerine, and cellulose—ordinary cotton or wood fibers—to form nitro-compounds. Thus, when nitric acid is heated with phenol or carbolic acid, $\text{C}_6\text{H}_5\text{OH}$, picric acid, or trinitrophenol, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, is formed. Or,



When nitric acid is heated with toluene, $\text{C}_6\text{H}_5\text{CH}_3$, *trinitrotoluene*, or *T. N. T.*, is formed:

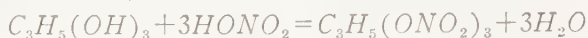


These substances are used as explosives. Trinitrotoluene may be said to be one of the safest and most powerful of all modern high explosives.

The actual manufacture of these substances is not so simple as it would appear from the above reactions and it is attended by more or less danger, depending upon the purity of the reacting substances, temperature control, etc. It will be noticed that 3 molecules of water are formed in each reaction and in order to remove this water as rapidly as it is formed, and so facilitate the reaction as far as speed and quantity of product are concerned, sulphuric acid is used, mixed with the nitric acid. Technically, a mixture of nitric and sulphuric acids is known as *mixed acid*.

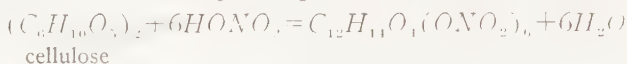
78. Glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$, which is a trihydric alcohol, reacts with nitric acid in a somewhat different manner. In this case, although the product formed is called *nitroglycerine*, it is really a nitrate of glycerine, the NO_3 group being present, as in

any nitrate, while in a nitro-compound the NO_2 , or nitro, group is present. Thus,



(See also U. S. P., page 407.)

Guncotton is made by the action of mixed acid on ordinary cotton; the reaction may be represented as follows:



NOTE TO THE STUDENT.—The reactions described in Art. 78 are not to be carried out by the student, because of the danger involved. Organic compounds, such as phenol, toluene, cellulose, and glycerine will be more fully described in *Organic Chemistry*.

THE ATMOSPHERE

A gaseous mixture. Specific gravity 1

79. Occurrence.—The aerial envelope that surrounds the earth and is of vital importance to all beings that live and breathe in it, is called the **atmosphere**. Its existence is demonstrated whenever it is set in motion, as exemplified by *winds*, which, when sufficiently violent, produce well-known and striking physical effects.

80. Properties.—Careful experiments have shown that, among other properties of matter, the atmosphere possesses weight. Regnault has shown that air, which has been chosen as the standard of specific gravity for gases, is 14.43 times heavier than hydrogen. Torricelli showed, in 1643, that the pressure of the air on the earth's surface would sustain a column of mercury about 76 centimeters in height; and, as a column of mercury of this height, with an area of 1 square centimeter, weighs 1,033 grammes, it follows that this weight represents the atmospheric pressure on every square centimeter of the earth's surface.

81. Composition.—The atmosphere consists chiefly of a mixture of nitrogen with $\frac{1}{5}$ volume of oxygen. In addition to these two elements, there are also present varying quantities of aqueous vapor, carbon dioxide, ammonia, and nitric acid; also,

traces of argon, neon, helium, krypton, and xenon. The average composition of the atmosphere is approximately shown in Table III.

TABLE III
COMPOSITION OF THE ATMOSPHERE

Oxygen	20.61 parts
Nitrogen, argon, etc.	77.95 parts
Carbon dioxide04 parts
Aqueous vapor	1.40 parts
Nitric acid	} Traces, according to the loca- tion—whether city, village, sea- shore, etc.
Ammonia	
Methane	
Hydrogen sulphide	
Sulphur dioxide, etc	

Although the proportion of oxygen in the air at a given spot may be diminished, and that of carbon dioxide increased by processes of oxidation (such as respiration and combustion) taking place there, the operations of wind and diffusion so rapidly mix the altered air with the greater general mass of the atmosphere, that the variations in the composition of air in different places are very slight.

82. Air a Mixture.—The fact that air is a mixture and not a chemical compound may be proved in numerous ways. In the first place, the oxygen and nitrogen are not present in any simple multiple of their atomic weights, which is necessary in all chemical compounds. Air also differs greatly from all compounds of these two elements known to chemists. If a mixture is made of nitrogen and oxygen in the proportion in which they exist in air, it will be found that no alteration of volume takes place, and that there is no increase of temperature; the mixture simply exhibits all the properties of ordinary atmospheric air.

The most conclusive evidence that these gases are mixed and not combined is that they may be separated by the action of water as a solvent. Oxygen is much more soluble than nitrogen, and if water that has been freed from gases by boiling is shaken with air and again boiled, the expelled gas is found, on analysis, to be much richer in oxygen than was the air, the oxygen amounting to about 34 per cent. of the dissolved gas.

CARBON

Symbol C. Atomic weight 12.005. Molecular weight 12.005. Valence II and IV.

83. Occurrence.—Carbon constitutes the most important constituent of all the organic substances. It occurs in the free state in nature in the two crystalline forms known as *diamonds* and *graphite*. When an organic compound is heated with a limited amount of air, a portion of the carbon remains as amorphous* carbon. Carbon also occurs in peat and lignite and in bituminous and anthracite coal. In combination with hydrogen, it occurs in mineral oils. It also occurs in the air as carbon dioxide, and in minerals and rocks in the form of a carbonate.

84. Preparation.—By heating wood or coal in a closed vessel, carbon in an impure state may be readily obtained. Water and volatile compounds of carbon with hydrogen and oxygen are driven off; the excess of carbon remains, together with the non-combustible portions of the wood or other body.

This process of heating a body and causing its decomposition, in part, into gaseous and liquid products, which are collected, is termed *destructive distillation*.

85. The Diamond.—The form of carbon known as a diamond is, when cut, a brilliant, transparent, and, usually, colorless solid; it has a specific gravity of 3.5 and is found in different crystalline forms. It is the hardest substance known, and can only be scratched or polished by rubbing it with diamond powder or dust. The colorless stones and those which are delicately tinted, are the most valuable. The black diamond, or *carbonado*, is used for grinding purposes and glass cutting. Mounted around the edge of a tube they are used for rock drilling, so that a cylindrical specimen of the entire rock strata can be obtained for examination. The diamond is a non-conductor of electricity.

*Amorphous means non-crystalline or without crystalline structure. Paraffin and beeswax are also common examples of amorphous substances.

Artificial diamonds were first made by Moissan, in 1887, who dissolved carbon in molten iron, which was subsequently chilled, causing an enormous pressure to be exerted upon the dissolved carbon. After thoroughly cooling, the mass was broken up and treated with acid to dissolve the iron, the insoluble residue being found to contain a few microscopic fragments, none larger than .5 mm. in diameter, which were recognized to be diamonds.

86. Graphite.—Graphite is found in large quantities in Siberia, India, Ceylon, and in the state of California.

Molten iron, containing silicon, *Si*, is capable of dissolving large quantities of carbon, which, upon the cooling of the iron, is deposited as graphite.

Graphite is now manufactured by heating a mixture of amorphous carbon, coke, charcoal, or anthracite, and a little sand in an electric furnace. Carbon alone, in one of its various forms, such as coke, charcoal, etc., cannot be converted into graphite, the change taking place through the intermediate formation of a carbide.

Graphite is a soft, shiny, grayish-black substance, smooth to the touch. It is usually found in compact laminated masses, but sometimes crystallized in six-sided plates. It has a specific gravity of 2.5 and is a good conductor of heat and electricity.

Graphite is used in the manufacture of lead pencils and plumbago crucibles; it is also used for glazing and for black polishing powder. Graphite may serve as a lubricant where oil cannot be used, on account of high temperatures, and also as a protective coating for ironwork.

87. Amorphous Carbon.—The modification of carbon known as **amorphous carbon** is formed by the carbonization of organic compounds. The amorphous carbon produced in this manner is named to indicate its origin or method of production. The principal forms are: (a) Coal, (b) lampblack, (c) wood charcoal, (d) animal charcoal, (e) gas carbon, and (f) coke.

(a) *Coal.*—The purest variety of *coal* is known as *anthracite*, which is an amorphous, black, hard, and somewhat lus-

trous body; is rather hard to ignite, and has lost all its organic structure. From this variety there is a regular graduation through *cannel* and *bituminous coals* of all varieties to *lignite*, or *brown coal*, which is sometimes only slightly altered wood. All coal is derived from primitive vegetation, changed and consolidated by heat and pressure. Anthracite is found where the strata have been most exposed to heat or disturbed by volcanic motions; bituminous, where the strata are nearly or quite horizontal, while brown coal is much more recent in age and retains elements of an organic structure.

(b) *Lampblack*.—Lampblack is the soot or amorphous carbon obtained by burning bodies rich in carbon with an insufficient supply of air. Resin or petroleum are burned with less



FIG. 10

air than is required for perfect combustion, the smoky products of this combustion passing into chambers hung with coarse cloths, on which the lampblack is deposited. The finest grades of lampblack are prepared by depositing the soot on metal cylinders revolving over the burners. Lampblack is purified by heating it in closed vessels.

Diamond black is an extremely pure quality of lampblack made by the imperfect combustion of natural gas, particularly that of the Ohio petroleum regions. Lampblack is used as a pigment for both oil and water colors as well as for liquid and drawing ink. It forms the chief ingredient in India ink and printing ink, and in the preparation of some kinds of leather.

(c) *Wood Charcoal*.—Wood charcoal is a form of carbon prepared from wood burned with but little access of air. Billets of wood are built up into a heap, Fig. 10, around stakes driven into the ground and the heap is then covered with earth or sand. The heap is fired at openings left at the bottom of the pile. For making fine charcoal, such as that of *willow charcoal*, the wood is burned in iron cylinders or retorts. In this method, which is a process of destructive distillation, the volatile products, such as wood spirits, pyroligneous acid, and tar, are collected.

Good charcoal has a pure black color, and a glittering fracture. It is used as a fuel, a polishing powder, an absorbent of gases and aqueous vapor; also, as a non-conductor of heat, as an ingredient in fireworks and in gunpowder. (See, also, U. S. P., page 101.)

(d) *Animal Charcoal*.—Animal charcoal, or *bone black*, is obtained by the calcining of bones in closed vessels. These vessels are either retorts, similar to those in which coal is distilled for the production of illuminating gas, or they are earthenware pots piled up in kilns and fired. After being burned the bones are ground in fluted rolls, and the dust removed.

Animal charcoal is a black, porous mass, used as a decolorizing and filtering agent in sugar refining and in other manufacturing processes.

(e) *Gas Carbon*.—Gas carbon, next to lampblack, is the purest form of amorphous carbon. It is formed, as its name implies, in the manufacture of coal gas and appears as an iron-gray deposit in the upper part of the retorts. Gas carbon is a good conductor of heat and electricity and is used for batteries and as carbons for electric arc lamps.

(f) *Coke*.—Coke is one of the products of the distillation of coal in ovens and retorts. It bears the same relation to coal as charcoal does to wood. Coke was originally produced by burning coal in heaps, with a limited supply of air. This occasioned a considerable loss of coal and led to the building of coke ovens, the coke produced in this way being found to be much harder, denser, and less combustible than that made in open heaps.

The most efficient method of coking is by means of coke ovens. There are many kinds of coke ovens, but the principle of operation and the object in view are the same in all. The simplest oven is the *beehive oven*, which is built of brick and is charged from the top from coal cars, running on rails on the top of a series of ovens. The volatile matter escapes through the charging openings, and the coke is removed through a door in the front of the oven. After the coal has been heated for about 36 hours the coke is raked out and quenched with water. The heat required to carry on the combustion is obtained by the burning of part of the coal and, in some plants, by the volatile, combustible gases which are given off.

The ovens most frequently used at the present time are the *by-product ovens*. These are more economical than the beehive ovens, as they utilize all of the gases given off and save the products of distillation of the coal.

88. Uses of Carbon.—The various kinds of carbon are employed for different purposes. Lampblack is used to a great extent in the preparation of inks and paints; gas carbon, or coke, is used in the electrical industries for electrodes, parts of batteries, etc.; wood charcoal is used in the manufacture of black powder; animal charcoal, or bone black, is often employed for filtering purposes, as it removes coloring matter, objectionable gases, and lead salts from drinking water. Large quantities are also used in the sugar industry to decolorize sugar solutions, and during the recent war, both wood and animal charcoals were used to a great extent as catalyzers in the manufacture of phosgene gas, and as absorbents for poisonous gases in the manufacture of gas masks in which charcoal made from fruit pits and coconut shells gave the best results.

89. The great differences in the properties exhibited by the diamond, graphite, and charcoal naturally lead to the belief that they consist of dissimilar carbon molecules. Very recent researches, however, have shown that the difference in the character and properties of these three varieties of carbon is due to differences in internal energy, the diamond having the most internal energy and charcoal having the least.

COMPOUNDS OF OXYGEN AND CARBON

CARBON DIOXIDE

Formula CO_2 . *Molecular weight* 44.005

90. Occurrence.—As has been stated, **carbon dioxide** is a constituent of the air, and, in certain localities, it is found issuing from the ground in large quantities. It is present in the soil, due to the decomposition of organic matter, and in combination with calcium it occurs in large quantities in limestone, marble, dolomite, magnesite, etc.

91. Preparation.—Carbon dioxide can be produced in a number of ways, of which only the following three methods will be considered:

1. By combustion of carbon with an excess of oxygen:



2. When limestone is heated, it is decomposed, the products of the decomposition being quicklime and carbon dioxide.



3. When limestone or marble, both consisting largely of calcium carbonate, are treated with dilute hydrochloric acid, HCl , the products formed are calcium chloride, $CaCl_2$, carbon dioxide, and water.



In this method, which is generally used in the laboratory, the gas is purified by passing it through a solution of sodium bicarbonate and then drying by passing it through a tube containing *fused*, or *anhydrous*, calcium chloride.

92. Physical Properties.—Carbon dioxide when pure is a colorless and odorless gas, one and a half times as heavy as air. At 0° C., 179.67 parts dissolve in 100 parts of water and at 20° C., 90.14 parts dissolve in 100 parts of water. Carbon dioxide may be liquefied, the liquid boiling at -78.2° C. It is shipped to the market in steel cylinders for use at soda fountains and in making carbonated waters.

93. Chemical Properties.—Carbon dioxide is a very stable compound, being only slightly decomposed at temperatures as high as $2,000^{\circ}$ C. It unites directly with the oxides of the alkalis, such as sodium and potassium oxides, to form the carbonates. Carbon dioxide is non-combustible and does not support combustion. Although the gas is poisonous, when inhaled in sufficient quantity, it does not possess toxic properties, but causes death by suffocation or by the exclusion of oxygen from the lungs. If a quantity of about 5 per cent. of the gas is present in air it will extinguish a lighted taper, but air containing this amount of the gas will support respiration for a short time.

CARBONIC ACID

Formula H_2CO_3 . Molecular weight 62.021

94. Preparation.—Carbonic acid is produced when carbon dioxide is dissolved in water.

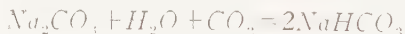


It is a weak acid and has not been isolated in the free state.

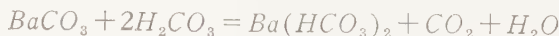
95. Salts of Carbonic Acid.—Although carbonic acid itself is very unstable, its salts, the *carbonates*, are very stable compounds. Being a dibasic acid, normal and acid salts are formed. When carbon dioxide is passed into solutions of the *alkali hydrates*, the normal carbonates, which are *soluble* in water, are formed according to the equation:



If these carbonates are again treated with carbon dioxide, the acid salt, or bicarbonate, is formed; thus:



The normal carbonates of the *alkaline earths*—barium, calcium, strontium, and lithium—can be prepared in the same way, but they are *insoluble* in water. The alkaline-earth carbonates dissolve in an excess of carbonic acid, forming the bicarbonates, which are soluble in water.



The quality of natural waters known as *hardness* is largely due to the presence of bicarbonates which they hold in solution. This hardness, if due entirely to the presence of bicarbonates, may be removed by boiling, and as the water loses its excess of carbon dioxide, the normal carbonates of the metals are precipitated.

96. Uses of Carbon Dioxide.—Gaseous carbon dioxide is used in large quantities in the manufacture of sodium bicarbonate, or baking soda, NaHCO_3 , and of the normal salt, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, or *washing soda*, and in the manufacture of *white lead*, which is a basic carbonate, $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$.

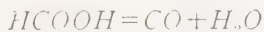
As mentioned above, the gas does not burn, and since a small percentage of it destroys the power of air to support combustion, it is used in fire-extinguishers that depend upon the action of sulphuric acid on a solution of sodium bicarbonate, carbon dioxide being liberated; thus:



CARBON MONOXIDE

Molecular formula CO . *Molecular weight* 28.005. *Specific gravity* .967.

97. Preparation.—Carbon monoxide may be made by passing a current of carbon dioxide over red-hot charcoal. In the laboratory, it is most conveniently prepared, however, by treating an organic compound, such as formic or oxalic acid, with concentrated sulphuric acid. Formic acid reacts as follows:



while oxalic acid gives,



If the second method is used, the gas must be passed through a solution of sodium or potassium hydroxide to remove the carbon dioxide. Fig. 11 shows the general arrangement of the apparatus.

The flask *A*, which contains the oxalic acid and the sulphuric acid, rests in a sand bath *B*, the evolved gas being sent

through a tube into the wash bottle *C* containing a solution of sodium hydroxide. The gas passes from here through a delivery tube into the inverted bottle, where it is collected over water in the usual manner.

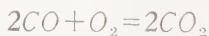
98. Physical Properties.—Carbon monoxide is a colorless, odorless, and tasteless gas. It is *very poisonous*. It has a specific gravity of .967, at 15° C., and is only slightly soluble in water; its critical temperature and pressure are, respectively, −139.5° C. and 35.5 atmospheres; it boils at −192° C. and the solid melts at −205.7° C.

99. Chemical Properties.—The chemical activity of carbon monoxide is due to the fact that the element carbon, in



FIG. 11

this compound, is bivalent and the compound is *unsaturated*, that is, the valence of carbon is not satisfied. The gas burns with a characteristic blue flame to carbon dioxide; thus,



It unites with chlorine to form phosgene, or carbonyl chloride, COCl_2 , and with sulphur to form carbon oxysulphide, COS , both compounds being gaseous at ordinary temperatures. It also unites with nickel and iron to form the *carbonyls* of these metals, $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$, both of which are liquids.

Carbon monoxide acts as a powerful reducing agent and is frequently used in metallurgical operations, for the production

of metals from their oxides. Thus, metallic oxides like Fe_2O_3 , CuO , etc. are converted into the metals at high temperatures. An ammoniacal solution of cuprous chloride, $CuCl$, absorbs carbon monoxide, a copper compound, $Cu_2Cl_2CO + 2H_2O$, which may be isolated, being formed. Carbon monoxide is devoid of acid properties and, consequently, is without action on lime water.

100. Water Gas.—Water gas is essentially a mixture of hydrogen and carbon monoxide and is used to a great extent, in this country, for heating and lighting purposes. Since the flame of water gas is itself not luminous, it was formerly necessary to *carburet*, or mix, the gas with the vapors of hydrocarbons rich in carbon, in order that it might be used for lighting purposes, but since the introduction of the incandescent gas mantle this *carburation* is unnecessary.

COMPOUNDS OF CARBON WITH CALCIUM AND SILICON

CALCIUM CARBIDE AND ACETYLENE

101. Calcium Carbide.—Calcium carbide, CaC_2 , is formed when lime and carbon are mixed in the proper proportions and heated to a high temperature; the lime is reduced and the metallic calcium unites with the carbon to form the carbide,



The reaction is carried out in an electric furnace.

102. Acetylene.—Acetylene, C_2H_2 , is prepared by the action of water on calcium carbide.



It is a colorless poisonous gas with a pleasant ethereal odor, when pure; but when mixed with impurities has a peculiar and disagreeable odor. It is condensable to a liquid at a pressure of 61.6 atmospheres and a temperature of $36.5^\circ C$. It is a non-supporter of combustion, and burns with a bright, lumi-

nous, but rather smoky flame. It is quite soluble in water, and is also readily absorbed by ammoniacal cuprous chloride, forming a red precipitate of cuprous acetylide that is explosive. This explosive body is sometimes formed in brass gas pipes by the action on them of the acetylene in coal gas, and may have been the cause of fatal accidents. It unites directly with the halogens; for example, the compounds of chlorine with it are: ethylene dichloride, $C_2H_2Cl_2$ and tetrachlorethane, $C_2H_2Cl_4$.

103. Carborundum.—The well-known abrasive carborundum is a carbide of silicon, and has the formula SiC . It is formed when silica, or sand, is heated in the electric furnace to a high temperature in contact with an excess of carbon.

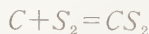


COMPOUNDS OF CARBON AND SULPHUR

CARBON DISULPHIDE

Formula CS_2 . *Molecular weight* 76.125

104. History and Preparation.—Carbon disulphide, also known as *carbon bisulphide*, was accidentally discovered by Lampadius in 1796. It is found in small quantities among the products of the destructive distillation of coal. It is formed, like the dioxide, by the direct union of its elements. It is prepared on a large scale by passing the vapor of sulphur over red-hot charcoal, the elements uniting according to the following equation:



Carbon disulphide may be prepared on a small scale in the laboratory by means of the apparatus shown in Fig. 12. The combustion tube, which should be about 2 feet long, is filled for about 3 inches from the sealed end with small pieces of sulphur; the rest of the tube is filled with small pieces of charcoal. The open end of the tube is connected with a glass tube dipping below the surface of water in a bottle placed in ice water. The

charcoal is heated to redness first and then the part containing the sulphur is heated. The sulphur vapor passes over the red-hot charcoal, combines with the carbon, and sulphur is deposited under the water in the receiver. The excess of sulphur and water are removed by distilling on a water bath.

In preparing carbon disulphide on a large scale, an upright cast-iron cylinder from 10 to 12 feet long and about 2 feet in diameter, and provided with a lid to admit of charging with charcoal, is used. The cylinder has a hopper near the bottom for the purpose of introducing the sulphur. The whole is heated from below. The sulphur vaporizes and combines with the red-hot carbon to form carbon disulphide, which is con-



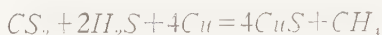
FIG. 14

densed in a long iron tube and collected under water in an iron basin. The impure material is then purified by distillation.

105. Physical Properties.—Carbon disulphide is a colorless liquid at ordinary temperatures, possessing, when pure, an agreeable, ethereal odor; traces of other compounds, however, give the commercially prepared compound a disagreeable odor. Carbon disulphide has a specific gravity of 1.292; at -116° C. and 78 atmospheres it freezes to a solid which melts at -110° C.; it boils at 46.2° C. The liquid is very inflammable, taking fire in the air at 150° C., burning with a blue flame, and producing carbon dioxide and sulphur dioxide, SO_2 , by its decomposition.

106. Chemical Properties and Uses.—Carbon disulphide is used in the arts as a solvent for pure rubber, or *caoutchouc*, and as a solvent for oils and fats. Frequently it is

employed for extracting the essential oils that contain the perfumes of roses, lavender, jasmine, etc. It also dissolves sulphur, phosphorus, and iodine, and is used to determine the moisture in commercial iodine. Is also frequently used as a starting point in the synthetic preparation of the hydrocarbons, because, if mixed with hydrogen sulphide and passed over copper filings heated to redness, methane is produced, thus:



When carbon disulphide is dissolved in alcohol and is acted on by ammonia with the aid of heat, ammonium sulphocyanide is formed according to the equation:



(See also U. S. P., page 528.)

CARBON TETRACHLORIDE

Formula CCl_4 . *Molecular weight* 153.85

107. Preparation and Uses.—Carbon tetrachloride is a colorless liquid at ordinary temperatures, having a specific gravity of 1.5817 and boiling at 76.7° C. It may be prepared by passing dry chlorine into carbon disulphide which contains a little iodine in solution:



As will be seen from the equation, a mixture of carbon tetrachloride and sulphur monochloride, S_2Cl_2 , is formed. These compounds are separated by fractional distillation, the latter being used in the vulcanization of rubber. Commercial carbon tetrachloride is largely used as a solvent for many organic compounds, it having a decided advantage over gasoline and benzine for this purpose, because of the fact that it is non-inflammable. Preparations used for removing spots from clothing and as general cleaning agents, are mixtures of carbon tetrachloride and benzine. Different types of fire-extinguishers contain carbon tetrachloride. When this compound comes in contact with burning material, it is immediately vaporized, the vapors displacing the air and stopping the combustion. (U. S. P., page 529.)

COMBINATION OF OXYGEN WITH HEATED GASES

COMBUSTION

108. Structure of Flame.—A **flame** is defined as a hot gas combining with oxygen at a temperature at which it becomes visible; that is, until it emits light. Some substances, like sulphur and phosphorus, give a flame when burned in air or in other gas, such substances being converted into gases or vapors at the temperature of combustion. The presence of a combustible gas or vapor is one of the necessary conditions for the existence of the flame. Thus, pure carbon burns without a flame and only becomes incandescent, because it is non-volatile. Similarly, a diamond or a piece of charcoal will burn in oxygen with a steady glow, but without flame, because it is not capable of conversion into vapor.

To obtain a brilliant light from a flame, it is essential that it should contain particles that are capable of incandescence, when highly heated. The flame of an oxyhydrogen blow-pipe is very pale, but when the flame is made to heat a column of lime, an intense light is obtained, due to the lime being heated to incandescence.

Phosphorus, when burning, emits a very luminous flame, owing to the oxide formed in the combustion being heated to incandescence.

From these statements it can be seen that the incandescent matter does not necessarily have to be a product of the combustion, as any solid in a finely divided state will confer illuminating power to a flame. If finely divided carbon is blown into a hydrogen flame from a bottle, fitted as shown in Fig. 13, the flame will be rendered highly luminous. The luminosity of most flames is due to the presence of highly heated carbon in

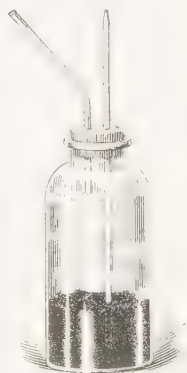


Fig. 13

a very minute state of division. Hydrogen and methane give pale flames, because they burn directly to carbon dioxide and water; on the other hand, ethylene and other hydrocarbons burn with a bright flame, because, at the temperature of combustion, they decompose into methane and carbon, and the particles of the latter become incandescent in the intense heat.



FIG. 14

109. Candle Flame.—When a candle is lighted, a portion of the wick burns until the heat reaches the wax of which the candle is made. This wax then melts and is drawn up into the wick and decomposed into various hydrocarbons, which ignite, combine with the oxygen of the air, and produce the flame. The flame, in turn, melts more of the wax around the wick and the process just described is repeated.

The structure of a candle flame is common to all flames obtained by the combustion of a gas. The flame of a candle consists of three cones, as shown in Fig. 14. The inner cone, which appears black, contains the unaltered gases. These cannot burn, because of the absence of air. The presence of unburned gases in this center cone can be shown by holding one end of a glass tube in this cone, when the gases will pass through the tube and may be ignited at the other end, as shown in Fig. 15. In the middle, or luminous, cone an imperfect combustion takes place. The gases break down, some



FIG. 15

burning completely, and the free carbon is heated to incandescence and gives luminosity to this part of the flame. The carbon is not burned, owing to the lack of sufficient oxygen for its combustion. The presence of free carbon in this cone is shown by lowering a porcelain plate on the cone, when a black film of soot will be deposited. The outer cone, or mantle, of the flame is very feebly luminous. In this cone, which is surrounded by air, the separated carbon burns completely, and the cone is termed the cone of perfect combustion.

The bright-blue cup surrounding the base of the flame is formed by the perfect combustion of a small portion of the hydrocarbons. Owing to the plentiful supply of air at this point, there is no separation of carbon.

110. Argand Burner. — As has been stated, all gas flames possess an identical structure, and by proper attention to the supply of air a flame fitted for either heating or illuminating can be obtained as desired.

For illuminating purposes the best results are obtained by what is known as the Argand burner, which is shown in Fig. 16. Air is admitted to

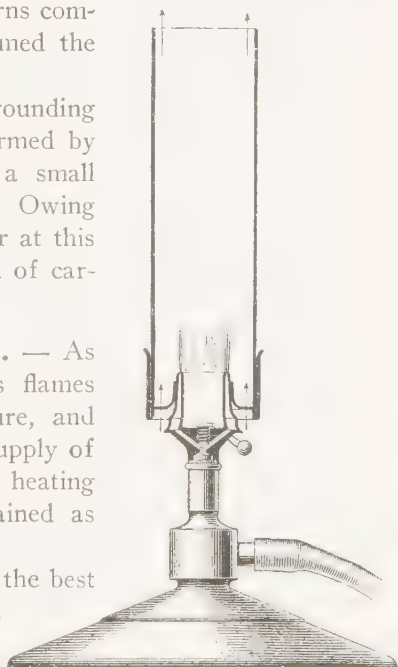


FIG. 16

the gaseous center of a ring-shaped flame, and the addition of a chimney, to produce a draft, insures great brilliancy and steadiness of the flame. In recent years a more brilliant flame for illuminating purposes is obtained by employing the heat of combustion for heating to incandescence an open-meshed mantle impregnated with a mixture of rare earths.

111. Bunsen Burner.—An excellent burner for heating purposes is the Bunsen burner, shown in Fig. 17. This consists

of a gas tube *a* projecting into the large mixing tube *b*. Air enters through the openings *c*, at the base of the burner, which are closed or opened by turning the collar *d*, thus regulating the supply of air. When a good supply of gas is turned on, a quantity of air, about double the volume of gas, is drawn in

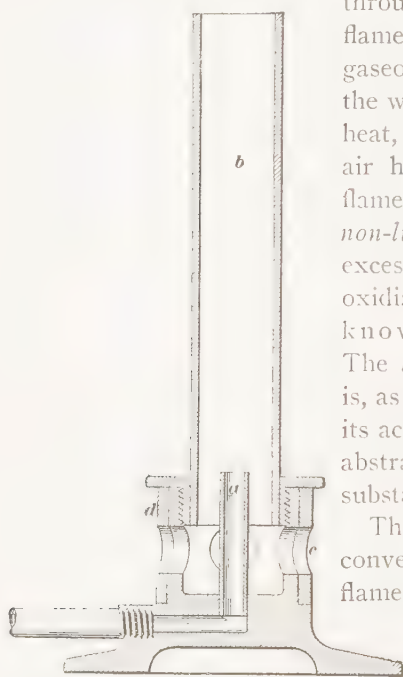


FIG. 17

through the openings *c*, and the flame, obtained by igniting the gaseous mixture at the orifice of the wide tube *b*, affords an intense heat, but no luminosity. If the air holes are closed, a luminous flame is at once produced. The *non-luminous flame* contains an excess of oxygen and is used for oxidizing purposes, hence is known as an *oxidizing flame*. The *luminous*, or *reducing*, flame is, as its name implies, reducing in its action, the glowing carbon in it abstracting oxygen from many substances containing it.

The luminous flame may be converted into a non-luminous flame, possessing considerable heating powers, by blowing a current of air from a jet into the flame. The instrument used for this purpose,

termed a *blowpipe*, is employed extensively in assaying.

112. Products of Combustion.—The products of combustion may be divided into two classes, namely, the *physical products*, such as light and heat, for the sake of which combustion is generally produced; and the *chemical products* that are to be conveyed away; these must be carbon dioxide and water, since the combustibles are composed of carbon and hydrogen.

EXPERIMENT.—That water is one of the chemical products of combustion may be readily proved by holding a cold, perfectly dry, bell jar over a candle flame; it will be noticed that it is at once bedewed with

moisture. If a little lime water is shaken in the jar, it will become milky, thus proving the presence of carbon dioxide. The same is true of respiration: a full breath blown through a glass tube into lime water will make it entirely white.

REMOVAL OF COMBUSTION PRODUCTS

113. Ventilation.—Pure air may be defined as air composed of nitrogen, oxygen, and carbon dioxide (about 3 parts in 10,000), together with some water vapor, ammonia, and hydrogen dioxide, but nothing of an injurious nature. The most common cause of the contamination of air is the combustion products of gas flames and the expiration products of

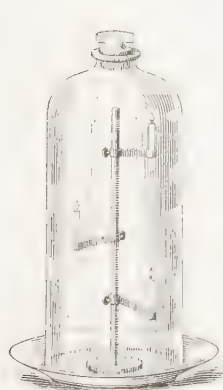


FIG. 18

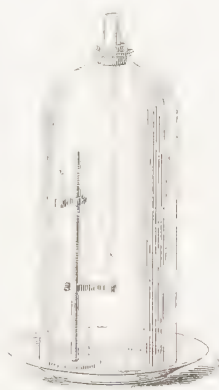


FIG. 19

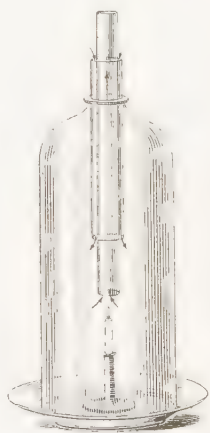


FIG. 20

human beings in rooms to which there is an inadequate supply of fresh air. The air issuing from the lungs of a human being at each expiration contains from 3 to 4 parts of carbon dioxide in each 100 parts of air, this gas being, in fact, produced by the combustion process taking place in the lungs. This amount could not be breathed again without danger, hence the necessity for a continued supply of fresh air to dilute the carbon dioxide sufficiently to render it no longer dangerous. The natural processes of respiration tend to raise the temperature of the air, thus causing it to expand and diminish its specific gravity, and causing it to ascend, and give place to fresh air. In order to

remove the vitiated air, a means of escape near the ceiling should be provided.

114. The principles of ventilation are usually illustrated by means of the apparatus shown in Figs. 18, 19, and 20. If lighted candles held at different heights are covered with a bell jar, as in Fig. 18, the warm carbon dioxide, formed by the burning candles, will accumulate in the upper part of the bell jar and will gradually extinguish the candles, the upper one being extinguished first. If, however, a glass tube is placed in the neck of the bell jar, so that the inner end is just slightly above the lower candle, as shown in Fig. 19, both candles will be extinguished. If the bell jar is raised slightly, so as to allow air to enter, the upper candle will go out and the lower one will continue to burn. The air entering below will replace the carbon dioxide formed, which will pass out through the tube. The same result can be accomplished by placing two tubes, one within the other, in the neck of the bell jar, Fig. 20. The products of combustion escape through the center tube, and fresh air enters through the space between the tubes, and the candle continues to burn.

INORGANIC CHEMISTRY FOR PHARMACY STUDENTS (PART 3)

CHEMICAL CALCULATIONS

PROPORTION, PERCENTAGE, AND CALCULA- TIONS OF QUANTITIES

INTRODUCTION

1. The Importance of Chemical Calculations.

Pharmacists must know how to solve chemical problems, for they enter into all laboratory and industrial operations. Every test, made to determine the percentage of a constituent in a material, can be completed only when one or more chemical problems have been solved, and every industrial operation in which chemistry is a factor is based on definite quantities of materials that can be determined, theoretically, only by solving chemical problems. Unless one knows how to solve chemical problems with accuracy, his efforts will be of little value, for he must determine percentages of constituents in materials, must calculate the amounts of materials needed to produce certain chemical changes, and must be able to tell, *theoretically*, how much of each product should be obtained from the change. It is, therefore, important that the methods of solving problems, described at this point, should be carefully studied and thoroughly understood.

PROPORTION

2. Fundamental Principles.—The mathematics involved in the solution of chemical problems consists essentially of the principles of *proportion*.

A **proportion** is an equality of ratios, the equality being indicated by the sign of equality (=). Thus, to write in the form of a proportion the two equal ratios, 6 : 9 and 10 : 15, one of the following forms may be employed :

$$6 : 9 = 10 : 15 \quad (1)$$

$$\frac{6}{9} = \frac{10}{15} \quad (2)$$

Either the first or the second form may be used. In this Section, the first form will be adopted, unless some statement can be made clearer by using the second form.

3. A proportion may be read in two ways. The old way to read the above proportion is, *6 is to 9 as 10 is to 15*; the new way is, *the ratio of 6 to 9 equals the ratio of 10 to 15*. Either way may be used, but the latter is to be recommended.

4. The numbers forming a proportion are called **terms**, and they are numbered consecutively from left to right, thus :

$$\begin{array}{cccc} \text{first} & \text{second} & \text{third} & \text{fourth} \\ 6 & : & 9 & = 10 : 15 \end{array}$$

In any proportion the ratio of the first term to the second term equals the ratio of the third term to the fourth term.

The first and fourth terms of a proportion are called the **extremes**, and the second and third terms, the **means**. Thus, in the foregoing proportion, 6 and 15 are the extremes and 9 and 10 are the means.

5. The correctness of a proportion may be tested by applying the following rule :

Rule.—*In any proportion, the product of the extremes equals the product of the means.*

Thus, in the proportion, 6 : 9 = 10 : 15, $6 \times 15 = 9 \times 10$, since both products equal 90.

If the proportion is written in the fractional form, as $\frac{6}{9} = \frac{10}{15}$, the terms must be multiplied in the manner indicated by the diagonal lines, as follows: $\frac{6}{9} \begin{smallmatrix} \nwarrow & \nearrow \\ \swarrow & \searrow \end{smallmatrix} \frac{10}{15}$. That is, $6 \times 15 = 9 \times 10$. In either case, the result is the same.

6. Problems in Proportion.—The problem that most frequently occurs in proportion is to find one of the terms, when the other three terms are given. Suppose the ratio 6 : 13 is given and, also, the first term, 30, of the second ratio, which term is the third term of the proportion and one of the means. The unknown term in a proportion is usually indicated by the letter x . The given ratios may, therefore, be written as the following proportion:

$$6 : 13 = 30 : x$$

The unknown extreme x may be found by the following rule:

Rule.—*To find an unknown extreme, divide the product of the means by the given extreme.*

Applying this rule to the preceding example,

$$x = \frac{13 \times 30}{6} = \frac{390}{6} = 65$$

7. If the unknown quantity is one of the mean terms, the following rule applies:

Rule.—*To find an unknown mean, divide the product of the extremes by the given mean.*

EXAMPLE.—The two ratios 17 : 51 and x : 42 are given. What is the value of the unknown term x ?

SOLUTION.—In this example, the terms 17 and 42 are the extremes, and 51 the given mean. Applying the rule,

$$x = \frac{17 \times 42}{51} = 14. \quad \text{Ans.}$$

8. In certain branches of chemical calculations a proportion is preferably stated in the form of a ratio, as $\frac{3}{9} = \frac{x}{30}$, x being the unknown quantity, as before. Applying the method explained in Art. 5, the following equation is obtained: $3 \times 36 = 9 \times x$. In order that the unknown quantity x may stand alone

on one side of the equality sign, both sides of the equation are divided by 9; thus, $\frac{3 \times 36}{9} = \frac{9x}{9} = x$.

Or,
$$x = \frac{3 \times 36}{9} = 12$$

EXAMPLE.—A given solution contains 12 parts of sugar to 44 parts of water. If in a solution of similar strength there are to be 96 ounces of water, how many ounces of sugar will be required?

SOLUTION.—Stated in the form of ratios, the equation may be written:

$$\frac{12}{44} = \frac{x}{96}. \quad \text{Applying the method of Art. 5, } 12 \times 96 = 44x. \quad \text{As just explained,}$$

$$\text{this may be written } x = \frac{12 \times 96}{44} = 26.17 \text{ oz.} \quad \text{Ans.}$$

9. As the application of proportion to problems in practice is of great importance to pharmacists, the application of the rules will be shown by the following examples:

EXAMPLE 1.—In a certain solution the ratio of alcohol to water is as 3 to 7. If the quantity of solution required is such that 13 ounces of alcohol are required, how many ounces of water must be added?

SOLUTION.—The given ratios are 3 : 7 and 13 : x . As the unknown quantity represents one of the extremes, the rule in Art. 6 must be applied.

$$\text{Hence, } x = \frac{7 \times 13}{3} = 30\frac{1}{3} \text{ oz.} \quad \text{Ans.}$$

EXAMPLE 2.—If there are 85 ounces of sugar in 131 ounces of syrup, how many ounces of sugar are required to make 30 ounces of syrup?

SOLUTION.—The given ratios are 85 : 131 and x : 30. The unknown quantity being one of the means, the rule in Art. 7 must be applied. Thus,

$$x = \frac{30 \times 85}{131} = 19.47 \text{ oz.} \quad \text{Ans.}$$

PERCENTAGE CALCULATIONS

10. Advantage of Percentage Calculations.—In certain operations pertaining to chemistry and pharmacy, it is very convenient to consider the quantity under consideration as being divided into 100 equal parts. Thus, instead of using the ordinary fractions $\frac{1}{4}$, $\frac{3}{5}$, and $\frac{2}{7}$, the equivalent fractions $\frac{25}{100}$, $\frac{60}{100}$, and $\frac{28\frac{1}{2}}{100}$ are used, or their equivalent decimals, .25, .60, and .286, respectively. The reason for this is that it is much

easier to compute with fractions whose denominators are 100 than it is to compute with fractions whose denominators are composed of other figures.

11. Definitions.—**Percentage** is a term applied to those arithmetical operations in which the number or quantity to be operated upon is supposed to be divided into 100 equal parts.

The term **per cent.** means *by the hundred*. Thus, 8 per cent. of a number means 8 hundredths, i. e., $\frac{8}{100}$, or .08, of that number; 8 per cent. of 250 is $250 \times \frac{8}{100}$, or $250 \times .08 = 20$; 47 per cent. of 75 ounces is $75 \times \frac{47}{100} = 75 \times .47 = 35.25$ ounces.

The **sign** of per cent. is %, and is read *per cent.* Thus, 6% is read *six per cent.*; $12\frac{1}{2}\%$ is read *twelve and one-half per cent.*, etc.

When expressing the per cent. of a number used in calculations, it is customary to express it decimally instead of fractionally. Thus, instead of expressing 6%, 25%, and 43% as $\frac{6}{100}$, $\frac{25}{100}$, and $\frac{43}{100}$, it is usual to express them as .06, .25, and .43, respectively.

12. Base, Rate Per Cent., and Percentage.—The different terms used in percentage calculations are: The *base*, the *rate* or *rate per cent.*, and the *percentage*.

The **base** is the number or quantity that is supposed to be divided into 100 equal parts.

The **rate per cent.** is that number of the 100 equal parts that is to be considered. The term *rate per cent.* is usually abbreviated to **per cent.** Thus, 7 per cent. is 7 parts of the 100 parts into which the quantity is supposed to be divided.

The **percentage** is the quantity obtained by taking the portion of the total quantity indicated by the per cent. Unless stated to the contrary, when a per cent. is given it is always understood to be *by weight*.

13. The following example will make the meaning of the terms clearer. Let it be supposed that 150 pounds of a 10 per cent. solution of phenol, or carbolic acid, is to be prepared. As the total quantity is supposed to be divided into 100 equal parts, it is necessary to ascertain how large each of these parts will be. Hence, on dividing 150 by 100, or $\frac{150}{100}$, it is found that each

part is equal to 1.5 pounds. As there is to be 10 per cent. of carbolic acid in the solution, there must be a quantity equal to $1.5 \times 10 = 15$ pounds. In this example, 150 pounds is the base, or total quantity; the per cent. is 10, and the percentage is 15 pounds.

14. Calculations Involving Per Cent. and Percentage.—In calculations relating to per cent. and percentage the following rules apply:

Rule I.—*To find the percentage, multiply the total weight of the mixture by the per cent. and divide by 100.*

Rule II.—*To find the per cent., multiply the percentage by 100 and divide by the weight of the mixture.*

Rule III.—*To find the weight of a mixture, multiply the percentage by 100, and divide the product by the per cent.*

EXAMPLE 1.—How many ounces of carbolic acid are there in 120 ounces of a 2 per cent. solution?

SOLUTION.—In this example, the weight of the mixture is equal to 120 ounces and the per cent. is 2; it is required to find the percentage of carbolic acid. Applying rule I, the percentage is $\frac{120 \times 2}{100} = 2.4$ oz. Ans.

EXAMPLE 2.—In 35 grains of cinchona there are 1.75 grains of quinine; what is the per cent. of quinine?

SOLUTION.—Applying Rule II, the per cent. is $\frac{1.75 \times 100}{35} = 5$. Ans.

EXAMPLE 3.—If only 2 ounces of sodium chloride is available, what quantity of a 5 per cent. solution can be made?

SOLUTION.—Applying rule III, the weight of the salt solution is $\frac{2 \times 100}{5} = 40$ oz. Ans.

15. Use of Atomic Weights in Problems.—Atomic weights are used to calculate the relative quantities, called *combining weights*, in which elements enter into compounds and in which substances enter into chemical changes. All chemical problems are based on the law of definite proportion, which states, as mentioned in *Inorganic Chemistry for Pharmacy Students*, Part I, that a chemical compound always contains the same constituents in the same proportion by weight.

Consider, for example, water, the formula of which is H_2O . This formula shows that each molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen. This fact is always true for water. By means of the atomic weights of these elements, one can calculate the weight relation between oxygen and hydrogen in water. The atomic weight of hydrogen, as shown in Table I, is 1.008, and that of oxygen is 16. The molecular weight of water is $(2 \times 1.008) + 16$, or 18.016. These values show that every 18.016 parts* of water contain 2.016 parts of hydrogen and 16 parts of oxygen. That is, the weight ratio of hydrogen to oxygen, in water, is 2.016 : 16, and 2.016 parts of hydrogen are needed to combine chemically with 16 parts of oxygen to produce 18.016 parts of water.

These parts by weight can be expressed in terms of any weight unit, such as grammes, pounds, tons, kilogrammes, etc. For instance, when grammes are used every 18.016 grammes of water contain 2.016 grammes of hydrogen and 16 grammes of oxygen; 2.016 grammes of hydrogen unite with 16 grammes of oxygen to produce 18.016 grammes of water, and the ratio of hydrogen to oxygen in 18.016 grammes of water is 2.016 grammes : 16 grammes.

These various weight relations, based on the atomic weights of elements, are used, as will be shown, to calculate problems and to arrive at information of value to chemical and pharmaceutical operations.

16. Calculating Per Cents. of Constituents in a Composition.—A chemist or a pharmacist must often calculate the per cent. of a constituent in a substance, using as a basis his knowledge of the chemical formula of the compound under consideration. He does this by applying atomic and molecular weights to the mathematical operations involved in calculating all percentages.

For illustration, suppose it is required to calculate the percentages of hydrogen and oxygen contained in water. By consulting a table of atomic weights it is found that the atomic

*The term *parts* will, unless otherwise specified, refer to *parts by weight*.

TABLE I
INTERNATIONAL ATOMIC WEIGHTS, 1921-22

Name	Symbol	Atomic Weight O = 16	Name	Symbol	Atomic Weight O = 16
Aluminum.....	<i>Al</i>	27.0	Molybdenum....	<i>Mo</i>	96.0
Antimony.....	<i>Sb</i>	120.2	Neodymium.....	<i>Nd</i>	144.3
Argon.....	<i>A</i>	39.9	Neon.....	<i>Ne</i>	20.2
Arsenic.....	<i>As</i>	74.96	Nickel.....	<i>Ni</i>	58.68
Barium.....	<i>Ba</i>	137.37	Niton.....	<i>Nt</i>	222.4
Bismuth.....	<i>Bi</i>	209.0	Nitrogen.....	<i>N</i>	14.008
Boron.....	<i>B</i>	10.9	Osmium.....	<i>Os</i>	190.9
Bromine.....	<i>Br</i>	79.92	Oxygen.....	O	16.00
Cadmium.....	<i>Cd</i>	112.40	Palladium.....	<i>Pd</i>	106.7
Cæsium.....	<i>Cs</i>	132.81	Phosphorus.....	<i>P</i>	31.04
Calcium.....	<i>Ca</i>	40.07	Platinum.....	<i>Pt</i>	195.2
Carbon.....	<i>C</i>	12.005	Potassium.....	<i>K</i>	39.10
Cerium.....	<i>Ce</i>	140.25	Praseodymium..	<i>Pr</i>	140.9
Chlorine.....	<i>Cl</i>	35.46	Radium.....	<i>Ra</i>	226.0
Chromium.....	<i>Cr</i>	52.0	Rhodium.....	<i>Rh</i>	102.9
Cobalt.....	<i>Co</i>	58.97	Rubidium.....	<i>Rb</i>	85.45
Columbium.....	<i>Cb</i>	93.1	Ruthenium.....	<i>Ru</i>	101.7
Copper.....	<i>Cu</i>	63.57	Samarium.....	<i>Sa</i>	150.4
Dysprosium.....	<i>Dy</i>	162.5	Scandium.....	<i>Sc</i>	45.1
Erbium.....	<i>Er</i>	167.7	Selenium.....	<i>Se</i>	79.2
Europium.....	<i>Eu</i>	152.0	Silicon.....	<i>Si</i>	28.1
Fluorine.....	<i>F</i>	19.0	Silver.....	<i>Ag</i>	107.88
Gadolinium.....	<i>Gd</i>	157.3	Sodium.....	<i>Na</i>	23.00
Gallium.....	<i>Ga</i>	70.1	Strontium.....	<i>Sr</i>	87.63
Germanium.....	<i>Ge</i>	72.5	Sulphur.....	<i>S</i>	32.06
Glucinum.....	<i>Gl</i>	9.1	Tantalum.....	<i>Ta</i>	181.5
Gold.....	<i>Au</i>	197.2	Tellurium.....	<i>Te</i>	127.5
Helium.....	<i>He</i>	4.00	Terbium.....	<i>Tb</i>	159.2
Holmium.....	<i>Ho</i>	163.5	Thallium.....	<i>Tl</i>	204.0
Hydrogen.....	<i>H</i>	1.008	Thorium.....	<i>Th</i>	232.15
Indium.....	<i>In</i>	114.8	Thulium.....	<i>Tm</i>	169.9
Iodine.....	<i>I</i>	126.92	Tin.....	<i>Sa</i>	118.7
Iridium.....	<i>Ir</i>	193.1	Titanium.....	<i>Ti</i>	48.1
Iron.....	<i>Fe</i>	55.84	Tungsten.....	<i>W</i>	184.0
Krypton.....	<i>Kr</i>	82.92	Uranium.....	<i>U</i>	238.2
Lanthanum.....	<i>La</i>	139.0	Vanadium.....	<i>V</i>	51.0
Lead.....	<i>Pb</i>	207.20	Xenon.....	<i>Xe</i>	130.2
Lithium.....	<i>Li</i>	6.94	Ytterbium.....	<i>Yb</i>	173.5
Lutecium.....	<i>Lu</i>	175.0	Yttrium.....	<i>Yt</i>	89.33
Magnesium.....	<i>Mg</i>	24.32	Zinc.....	<i>Zn</i>	65.37
Manganese.....	<i>Mn</i>	54.93	Zirconium.....	<i>Zr</i>	90.6
Mercury.....	<i>Hg</i>	200.6			

weight of hydrogen is 1.008 and that of oxygen is 16. These facts afford a basis for calculating the molecular weight of water. Each molecule of water consists of 2 atoms of hydrogen and 1 atom of oxygen. The molecular weight is, therefore, $(2 \times 1.008) + 16$, or 18.016.

He next calculates the percentage of one of the constituents present, as, for instance, hydrogen. He knows from the atomic and molecular weights that 18.016 parts of water contain 2.016 parts of hydrogen. In this case the 18.016 parts of water represent the total weight of the compound and the 2.016 parts of hydrogen, the percentage. The per cent. of hydrogen represented by this quantity may be calculated by applying Rule II, Art. 14. Thus, the per cent. of hydrogen is equal to $\frac{2.016 \times 100}{18.016} = 11.19$. That is, in 100 parts of water there are 11.19 parts of hydrogen.

The per cent. of oxygen is calculated by applying the same rule. Thus, $\frac{16 \times 100}{18.016} = 88.81$ per cent. of oxygen. That is, water contains 88.81 per cent. of oxygen.

17. The method used for calculating the per cent. of hydrogen and of oxygen contained in water is applied to all similar problems. But, in applying rule II, Art. 14, to this special class of problems, it may be modified so as to apply more directly and obviate any preliminary calculations. This modified rule is as follows:

Rule.—*To find the per cent. by weight of an element in a chemical compound, multiply the atomic weight of the element by the number of atoms of that element in a molecule of the compound and also by 100, and then divide the product by the molecular weight of the substance.*

This rule may also be expressed as a formula. Thus,

$$\frac{\text{The per cent. of an element in a compound} = \text{number of atoms of the element in the compound} \times \text{atomic weight of the element} \times 100}{\text{molecular weight of the compound}}$$

EXAMPLE.—The formula for potassium chlorate is $KClO_3$. What is the per cent. of each element in the compound?

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SOLUTION.—It is first necessary to find the molecular weight of the compound.

Each molecule of $KClO_3$ contains 1 atom of potassium, 1 of chlorine, and 3 of oxygen. Hence, the molecular weight is calculated by means of the atomic weights of the elements, as follows:

$$1 \times 39.10 = 39.10, \text{ for potassium}$$

$$1 \times 35.46 = 35.46, \text{ for chlorine}$$

$$3 \times 16.00 = 48.00, \text{ for oxygen}$$

Total, 122.56 = the molecular weight of potassium chlorate.

Applying the preceding rule or formula, the per cent. of each element is found in the following manner:

$$\text{Per cent. of potassium} = \frac{1 \times 39.10 \times 100}{122.56} = \frac{3,910.00}{122.56} = 31.90, \text{ nearly. Ans.}$$

$$\text{Per cent. of chlorine} = \frac{1 \times 35.46 \times 100}{122.56} = \frac{3,546.00}{122.56} = 28.93, \text{ nearly. Ans.}$$

$$\text{Per cent. of oxygen} = \frac{3 \times 16.00 \times 100}{122.56} = \frac{4,800.00}{122.56} = 39.17, \text{ nearly. Ans.}$$

The calculation may be checked by finding the sum of the various per cents., which should be equal to 100.

EXAMPLE 2.—Ferric oxide has the formula Fe_2O_3 . What per cent. of iron is present in the compound?

SOLUTION.—Each molecule of ferric oxide contains 2 atoms of iron and 3 of oxygen. The molecular weight is, therefore, found as follows:

$$2 \times 55.84 = 111.68, \text{ for iron}$$

$$3 \times 16.00 = 48.00, \text{ for oxygen}$$

Total, 159.68 = the molecular weight of ferric oxide.

Applying the rule, the per cent. of iron is,

$$\frac{2 \times 55.84 \times 100}{159.68} = \frac{11,168.00}{159.68} = 69.94, \text{ nearly. Ans.}$$

EXAMPLE 3.—What per cent. of copper is contained in copper sulphate, $CuSO_4 \cdot 5H_2O$?

SOLUTION.—Each molecule of copper sulphate contains 1 atom of copper, 1 of sulphur, 9 of oxygen, and 10 of hydrogen. The molecular weight is, therefore, found as follows:

$$1 \times 63.57 = 63.57, \text{ for copper}$$

$$1 \times 32.06 = 32.06, \text{ for sulphur}$$

$$9 \times 16.00 = 144.00, \text{ for oxygen}$$

$$10 \times 1.008 = 10.08, \text{ for hydrogen}$$

Total, 249.71 = molecular weight of copper sulphate.

The per cent. of copper is found by applying the preceding rule. Thus,

$$\frac{1 \times 63.57 \times 100}{249.71} = 25.46, \text{ nearly. Ans.}$$

18. It is sometimes necessary to calculate the per cent. of a constituent consisting of more than one element. In such cases the molecular weight of the constituent is used in the rule, Art. **17**. The following examples will illustrate the method to be followed:

EXAMPLE 1.—Calculate the per cent. of calcium oxide, or lime, CaO , contained in calcium carbonate, $CaCO_3$.

SOLUTION.—The molecular weight of calcium carbonate is found in the manner previously described. Thus,

$$1 \times 40.070 = 40.070, \text{ for calcium}$$

$$1 \times 12.005 = 12.005, \text{ for carbon}$$

$$3 \times 16.000 = 48.000, \text{ for oxygen}$$

$$\text{Total, } 100.075 = \text{molecular weight of calcium carbonate.}$$

The molecular weight of calcium oxide must also be found. Thus,

$$1 \times 40.070 = 40.070, \text{ for calcium}$$

$$1 \times 16.000 = 16.000, \text{ for oxygen}$$

$$\text{Total, } 56.070 = \text{molecular weight of calcium oxide.}$$

The latter weight is now substituted in the formula, Art. **17**, for the atomic weight of the element considered. Thus, the per cent. of calcium

$$\text{oxide in calcium carbonate is: } \frac{1 \times 56.07 \times 100}{100.075} = 56.03, \text{ nearly. Ans.}$$

EXAMPLE 2.—Calculate the per cent. of carbon dioxide, CO_2 , in sodium carbonate, Na_2CO_3 .

SOLUTION.—The molecular weight of sodium carbonate is found in the following manner:

$$2 \times 23.00 = 46.000, \text{ for sodium}$$

$$1 \times 12.005 = 12.005, \text{ for carbon}$$

$$3 \times 16.000 = 48.000, \text{ for oxygen}$$

$$\text{Total, } 106.005 = \text{molecular weight of sodium carbonate.}$$

The molecular weight of carbon dioxide is:

$$1 \times 12.005 = 12.005, \text{ for carbon}$$

$$2 \times 16.000 = 32.000, \text{ for oxygen}$$

$$\text{Total, } 44.005 = \text{molecular weight of carbon dioxide.}$$

Applying the formula, Art. **17**, the per cent. of carbon dioxide is

$$\frac{1 \times 44.005 \times 100}{106.005} = 41.51, \text{ nearly. Ans.}$$

19. General Method for Calculating the Per Cent. of a Constituent in a Compound.—The preceding explanations and problems show that the following steps must be

taken in calculating the per cent. of a constituent contained in a compound.

1. Calculate the molecular weight of the compound.
2. Calculate the molecular weight of the constituent, if the latter consists of more than one element.
3. If the constituent consists of one element, apply the following formula:

$$\text{Per cent. of a constituent in a compound} = \frac{\text{number of atoms of the element in the compound} \times \text{atomic weight of the element} \times 100}{\text{molecular weight of the compound}}$$

4. If the constituent consists of more than one element, apply the following formula:

$$\text{Per cent. of a constituent in a compound} = \frac{\text{number of groups of the constituents in the compound} \times \text{molecular weight of the constituent} \times 100}{\text{molecular weight of the compound}}$$

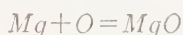
CALCULATING QUANTITIES OF CONSTITUENTS

20. To Calculate Quantities in Chemical Problems.—Pharmacists may be required to calculate the relative quantities of substances needed to produce certain chemical changes and of the products formed. Chemical equations representing the changes are used as a basis for these calculations, and as they must be properly written, if the calculation is to be correct, a review of the methods for ascertaining whether an equation is correct will, at this point, be helpful.

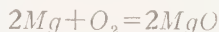
First of all, a chemical equation is not correct unless it represents a change that actually takes place and can be reproduced. Likewise, the quantities by weight of the materials used must never be greater nor less than the quantities by weight of the materials produced, for matter can be neither created nor destroyed. In other words, the sum of the combining weights, calculated from the atomic weights of the elements involved, on one side of the equation must equal the sum of the combining weights on the other. Finally, the number of atoms of any element on one side of an equation must equal the number of atoms of that element on the other side. If a chemical equation meets all of these requirements, it is correctly written and can

be used as a basis for the calculation of quantities involved in chemical changes.

As an illustration, consider the change that takes place when magnesium, Mg , is burned to form magnesium oxide, MgO . The valence of magnesium is 2 and that of oxygen is 2. Hence, 1 atom of magnesium is needed to unite with 1 atom of oxygen, thus:

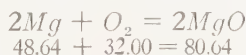


This equation is not correct, however, because oxygen always exists in nature as a molecule, O_2 , and not as an atom, O , as shown in this equation. Doubling the quantities in the equation will show oxygen as a molecule, thus:



21. The combining weights, atomic or molecular, of the substances used and produced are next calculated from the atomic weights of the various elements involved. As the atomic weight of magnesium = 24.32, it follows that 2 atoms of magnesium, $2Mg$, have a combining weight of $2 \times 24.32 = 48.64$. The atomic weight of oxygen = 16; then 2 atoms of oxygen contained in 1 molecule of oxygen, O_2 , have a combining weight of 32.0. The molecular weight of magnesium oxide, containing 1 atom of magnesium and 1 of oxygen, equals the sum of the atomic weights of magnesium and oxygen, 24.32 and 16, or 40.32. The equation shows 2 molecules of magnesium oxide; it has a combining weight, therefore, of 2×40.32 , or 80.64.

The combining weights of the substances involved in a chemical change are, for convenience, placed under the respective formulas and symbols of the substances, thus:



This equation shows that 48.64 parts by weight of magnesium unite with 32.0 parts of oxygen to form 80.64 parts of magnesium oxide; that 32.0 parts of oxygen unite with 48.64 parts of magnesium to produce magnesium oxide; that 48.64 parts of magnesium form 80.64 parts of magnesium oxide when burned; that the sum of the weights of magnesium

and oxygen, combined chemically, equals the weight of magnesium oxide formed.

22. So far, the equation $2Mg + O_2 = 2MgO$ has met two of the requirements of a correctly written chemical equation; it represents a change that can be produced by burning magnesium, and the sum of the combining weights on one side of the equation is equal to that on the other. Likewise, it meets the third requisite, for there are 2 atoms of magnesium and 2 of oxygen on each side of the equation. Hence, the equation is correctly written and can be used as a basis for calculations involving the chemical combination between magnesium and oxygen.

For instance, a pharmacist may be asked how much magnesium oxide is produced when 100 pounds of magnesium are burned. Problems such as this one are based primarily on the fact that the combining weights of substances entering into a change are directly proportional to the exact quantities of these substances. This fact can be expressed as a proportion, thus:

The ratio of the combining weight of one substance to its weight equals the ratio of the combining weight of the substance formed to its weight.

In the process of burning magnesium to form magnesium oxide, the ratios representing the reaction may be written as follows:

$$\frac{48.64}{100 \text{ lbs.}} \quad \frac{80.64}{x} \\ 2Mg + O_2 = 2MgO$$

When the reaction that takes place and the values of the combining weights are represented in this manner, it is a simple matter to write the correct proportion. In the preceding statement representing the reaction, there are two ratios which are to form a proportion. Arranging these ratios as a proportion, it

will assume the following form: $\frac{48.64}{100} = \frac{80.64}{x}$

Solving the proportion according to the method shown in Arts. 5 and 8, the following equation is obtained:

$$48.64x = 80.64 \times 100 \\ \therefore \frac{80.64 \times 100}{48.64} = 165.79 \text{ lb. of } MgO. \quad \text{Ans.}$$

If preferred, the ratios $\frac{48.64}{100} = \frac{80.64}{x}$ may be arranged as in the following proportion:

$$48.64 : 100 = 80.64 : x$$

Applying the rule in Art. 6, the value of x is found as follows:

$$x = \frac{80.64 \times 100}{48.64} = 165.79 \text{ lb. of } MgO. \text{ Ans.}$$

23. General Method for Solving Problems Involving Weights of Chemicals.—The calculation of weights of elements and compounds involved in chemical changes may be simplified by performing the various steps of the calculation in the following order.

1. *Write the chemical equation representing the change.* It should be noted with reference to this equation that some equations may be written down by applying the valence principles. Others, that represent reactions not following the general rule, must be written down from memory or secured from textbooks. In every case, an equation merely represents a change that has been found by tests to take place.

2. *Check the accuracy of the equation by noting whether it meets all the requirements of a correctly written equation.*

3. *Calculate the combining weights of the substances involved in the problem and place these weights over the proper symbols in the equation.*

4. *Arrange the known and the unknown values as ratios and calculate the unknown value by means of the rules given in Arts. 5 and 8.*

24. The application of the preceding method of calculation will be shown by the following examples:

EXAMPLE 1.—Calculate the weights of sodium chloride, $NaCl$, and sulphuric acid, H_2SO_4 , required to produce 100 kilogrammes of sodium sulphate, Na_2SO_4 .

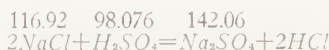
SOLUTION.—The first step in the solution of the problem is to write the equation representing the reaction. Thus,



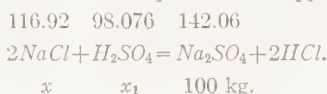
It is seen that three substances—sodium chloride, sulphuric acid, and sodium sulphate—must be considered in the solution, the fourth sub-

stance, hydrochloric acid, HCl , being left out of consideration, as it is not required.

According to Art. 23, the next step is to calculate the combining weights of the substances and place them over the corresponding formula in the equation. Thus,



The required weight of sodium sulphate is 100 kilogrammes, so this weight is written under its formula in the equation. As the weights of the sodium chloride and the sulphuric acid are to be found, these weights are, for the present, indicated by the symbols x and x_1 in the equation. In its present form the equation will appear as follows:



Omitting the formulas, for reasons of clearness, the given ratios may be stated in the following manner:

$$\frac{116.92}{x}, \frac{98.076}{x_1}, \text{ and } \frac{142.06}{100}$$

Each one of the unknown ratios is now combined with the known ratio, $\frac{142.06}{100}$, as a proportion in order to find the values of x and x_1 .

Thus, to calculate the weight of sodium chloride required, the following proportion is written:

$$\frac{116.92}{x} = \frac{142.06}{100}$$

Solving, as in Art. 8, $142.06x = 116.92 \times 100$.

$$x = \frac{116.92 \times 100}{142.06} = 82.3 \text{ kg. of } NaCl$$

Similarly, to calculate the weight of the sulphuric acid, the second ratio is employed.

Thus,
$$\frac{98.076}{x_1} = \frac{142.06}{100}$$

$$142.06x_1 = 98.076 \times 100$$

$$x_1 = \frac{98.076 \times 100}{142.06} = 69.04 \text{ kg. of } H_2SO_4$$

It follows that to produce 100 kg. of sodium sulphate there are required 82.3 kg. of sodium chloride and 69.04 kg. of sulphuric acid.

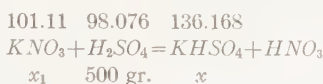
Ans.

EXAMPLE 2.—Potassium acid sulphate, $KHSO_4$, in addition to nitric acid may be produced by adding sulphuric acid to potassium nitrate, KNO_3 . If 500 grammes of H_2SO_4 are available, how many grammes of

$KHSO_4$ may be produced, and how many grammes of KNO_3 are required?

SOLUTION.—The formula, together with the combining weights, the unknown terms, and the given term, are written as in the last example.

Thus,



The three ratios may be written,

$$\begin{array}{ccccc} 136.168 & 101.11 & & 98.076 & \\ x & , & x_1 & , \text{ and} & 500 \end{array}$$

Combining each unknown ratio in turn with the known one, the following proportions may be written:

$$\frac{136.168}{x} = \frac{98.076}{500}$$

and

$$\frac{101.11}{x_1} = \frac{98.076}{500}$$

It follows that $98.076x = 136.168 \times 500$.

$$x = \frac{136.168 \times 500}{98.076} = 694.19 \text{ Gm.}$$

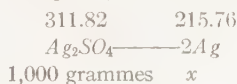
Also,

$$\begin{array}{l} 98.076x_1 = 101.11 \times 500 \\ x_1 = \frac{101.11 \times 500}{98.076} = 515.46 \text{ Gm.} \end{array}$$

Hence, if 515.46 Gm. of potassium nitrate are added to 500 Gm. of sulphuric acid, 694.19 Gm. of potassium acid sulphate are produced. Ans.

EXAMPLE 3.—How many grammes of silver, Ag , can be obtained from 1,000 grammes of silver sulphate, Ag_2SO_4 ?

SOLUTION.—The molecular weight of Ag_2SO_4 is 311.82. The atomic weight of Ag is 107.88. It follows that $2Ag = 107.88 \times 2 = 215.76$. The formulas, with the corresponding molecular weights, as well as the required weight of silver sulphate, are as follows:



The following ratios may now be written:

$$\frac{311.82}{1,000} = \frac{215.76}{x}$$

Hence,

$$\begin{array}{l} 311.82x = 215.76 \times 1,000 \\ x = \frac{215.76 \times 1,000}{311.82} = 691.94 \text{ Gm. Ans.} \end{array}$$

25. Application of Preceding Formulas and Rules.

It is important to acquire familiarity with the solution of

chemical problems. For this purpose all kinds of problems should be solved in such a way that every step is clearly understood, so that problems of a similar nature may be easily recognized when met with in industrial work. Following are examples for practice that will serve to meet these requirements, if they are solved in such a manner that each step is well understood.

EXAMPLES FOR PRACTICE

1. Calculate the per cents. composition of potassium acid sulphate, $KHSO_4$.

$$\text{Ans. } \begin{cases} K=28.714\% \\ H=0.740\% \\ S=23.544\% \\ O=47.000\% \end{cases}$$

2. Calculate the per cents. composition of calcium chloride, $CaCl_2$.

$$\text{Ans. } \begin{cases} Ca=36.103\% \\ Cl=63.897\% \end{cases}$$

3. Calculate the per cents. composition of borax, $Na_2B_4O_7$.

$$\text{Ans. } \begin{cases} Na=22.77\% \\ B=21.78\% \\ O=55.45\% \end{cases}$$

4. What quantity of lime, CaO , can be obtained from 1,000 pounds of calcium carbonate, $CaCO_3$?

$$\text{Ans. } 560.25 \text{ lb.}$$

5. How much ferric chloride, $FeCl_3$, may be obtained from 100 pounds ferric hydroxide, $Fe(OH)_3$?

$$\text{Ans. } 151.8 \text{ lb.}$$

6. What per cent. of sulphur trioxide, SO_3 , is contained in barium sulphate, $BaSO_4$?

$$\text{Ans. } 34.2\%$$

7. Zinc chloride, $ZnCl_2$, may be made by treating zinc oxide, ZnO , with hydrochloric acid, HCl . The reaction is represented by the following equation: $ZnO + 2HCl = ZnCl_2 + H_2O$. (a) How much ZnO will react with 100 kilogrammes of HCl ? (b) How much HCl will be necessary to make 150 kilogrammes of $ZnCl_2$?

$$\text{Ans. } \begin{cases} (a) 111.56 \text{ kg.} \\ (b) 80.27 \text{ kg.} \end{cases}$$

8. The reaction between ammonium chloride, NH_4Cl , and lime, CaO , may be represented by the equation, $2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$. How much lime will be required to make 30 pounds of ammonia, NH_3 ?

$$\text{Ans. } 49.4 \text{ lb.}$$

SOLUTIONS AND THEIR IONIZATION

SOLUTIONS

CLASSIFICATION

26. Emulsions, Colloidal Suspensions and Solutions.—A substance mixed with a liquid may result in a suspension of the substance, in a finely divided state, throughout the liquid or in the disappearance of the substance into the liquid with the formation of a clear, transparent, homogenous mixture, which does not separate into its constituents, no matter how long it may be allowed to stand. The latter mixture is a true **solution**; the substance dissolved is the **solute**, and the dissolving liquid, the **solvent**.

If the substance is a liquid that is suspended throughout the liquid in droplets, the mixture is called an **emulsion**. Butter fat and some other constituents form milk, which is an emulsion. (U. S. P., pages 136, 137, and 138.)

If the substance is a solid suspended in so finely divided a condition throughout the liquid that the mixture is not made noticeably cloudy and the solid does not settle out even after long standing, and yet does not form a true solution, a *colloidal suspension* or *colloidal solution* is formed and the solid forming it is called a **colloid**. Starch, glues, and gums are typical colloids.

Colloidal suspensions and emulsions should not be confused with true solutions. In time, constituents in an emulsion separate from each other. Colloidal suspensions differ from solutions in that rays of light passing through colloidal suspensions become visible, similar to a sunbeam in a dark, dusty room, but when passing through a true solution they are invisible.

VARIATIONS IN SOLUBILITY

27. Solubility of Substances.—The thought naturally arises as to whether there is any limit to the quantity of a substance that may be dissolved in a given quantity of solvent. Some liquids can be dissolved in other liquids in unlimited proportions, as, for example, alcohol in water. Potassium chlorate, $KClO_3$, will form a solution when added to 100 cubic centimeters of water at $18^\circ C.$, until 6.6 grammes of it have been introduced, but no quantity beyond this amount will dissolve in this amount of water. In fact, most solids may be dissolved in a liquid only up to a certain limit, which varies from scarcely perceptible quantities up to large amounts.

A solution in which a solvent will dissolve no more of the solute under existing conditions, even when in contact with some of the undissolved substance used as the solute, is called a **saturated solution**. The ratio of the weight of a solute to the weight of a solvent, saturated by the solute at a given temperature, is known as the **solubility** of the solute.

28. Table II shows the solubility of several common substances in 100 cubic centimeters of water at $18^\circ C.$ The table is divided into a number of vertical and horizontal rows. On top of the vertical rows are placed a given number of elements representing the positive radicals of the substances, and at the left of the horizontal rows are placed a number of groups of elements indicating the negative radicals. The number in the square, at which two rows intersect, shows the number of grammes of the various substances soluble in 100 cubic centimeters of water at $18^\circ C.$ For instance, the square at which the rows headed K and Cl intersect contains the number 32.95, which represents the number of grammes of potassium chloride, KCl , soluble in 100 cubic centimeters of water at $18^\circ C.$ Again the rows headed Mg and SO_4 intersect at the number 35.43. The combination of the symbols Mg and SO_4 represents the compound magnesium sulphate, $MgSO_4$, and the number 35.43 indicates the number of the grammes of this compound soluble in 100 cubic centimeters of water at $18^\circ C.$

TABLE II
WEIGHT, IN GRAMMES, OF SUBSTANCES SOLUBLE IN 100 C. C. OF WATER AT 18° C.

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95	35.86	77.79	.00013	.3	37.24	51.09	73.19	55.81	203.9	1.49
Br	65.86	88.76	168.7	.00001	.042	103.6	96.52	143.3	103.1	478.2	.598
I	137.5	177.9	161.5	.00000035	.006	201.4	169.2	200.0	148.2	419.0	.08
F	92.56	4.44	.27	195.4	72.05	.16	.012	.0016	.0087	.005	.06
NO ₃	30.34	83.97	71.43	213.4	8.91	8.74	66.27	121.8	74.31	117.8	51.66
ClO ₄	6.6	97.16	313.4	12.25	3.69	35.42	174.9	179.3	126.4	183.9	150.6
BrO ₃	6.38	36.67	152.5	.59	.30	.8	30.0	85.17	42.86	58.43	1.3
IO ₃	7.62	8.33	80.43	.004	.059	.05	.25	.25	6.87	.83	.002
OH	142.9	116.4	12.04	.01	40.04	3.7	.77	.17	.001	.0005	.01
SO ₄	11.11	16.83	35.64	.55	4.74	.00023	.011	.20	35.43	53.12	.0041
CrO ₄	63.1	61.21	111.6	.0025	.006	.00035	.12	.4	73.0		.00002
C ₂ O ₄ *	30.27	3.34	7.22	.0035	1.48	.0085	.0046	.00055	.03	.00064	.00016
CO ₃	108.0	19.39	1.3	.003	4.95	.0023	.0011	.0013	.1	.004	.0001

*Oxalates.

EFFECT OF TEMPERATURE ON SOLUBILITY

29. Solubility of Solids and Gases as Affected by Temperature.—Temperature has an important bearing on the solvent action of liquids, usually *increasing* it as the temperature *rises*, when the solute is a *solid*; and *decreasing* it as

TABLE III
SOLUBILITY OF GASES IN WATER

Name of Substance	By Volume			By Weight		
	0° C.	15° C.	100° C.	0° C.	15° C.	100° C.
Acetylene.....	1.73	1.15		.20	.13	
Air.....	.02881	.02045	.01105	.02936	.02090	
Ammonia.....	1298.9	802.4		98.7	60.6	
Carbon dioxide..	1.713	1.019		.3347	.1971	
Carbon mon- oxide.....	.03537	.02543	.0141	.0044	.0031	
Chlorine.....	4.61	2.635		1.46	.8493	
Hydrogen chlo- ride.....	506.5	461.5		82.5	75.2	
Hydrogen.....	.0203	.0183	.0166	.00018	.00016	
Hydrogen sul- phide.....	4.686	3.056		.710	.458	
Methane.....	.05563	.03690	.0170	.00396	.00260	
Nitrogen.....	.02388	.01786	.01	.00298	.00221	
Oxygen.....	.0489	.03415	.017	.00695	.0048	
Sulphur dioxide.	79.789	47.276		22.83	13.54	

the temperature *rises*, when the solute is a *gas*. Table III shows the solubility of some gases in water at 0° C., 15° C., and 100° C.

The term By Volume employed in Table III means the volume of the gases, at a temperature of 0° C. and a pressure of 760 mm., that may be dissolved by 1 volume of water. The term By Weight means the number of grammes of gas dissolved by 100 grammes of water. For example, the table shows that .0489 volume of oxygen is dissolved in 1 volume of water at 0° C. to form a saturated solution, and that .00695 gramme

of oxygen is dissolved in 100 grammes of water at 0° C. to form a saturated solution.

30. Supersaturated Solutions.—If a solution, saturated at a high temperature, is allowed to cool, less solute can be held in solution and the excess will usually deposit from the solution, maintaining saturation at the various temperatures. Sometimes the solute fails to crystallize out as the temperature falls, particularly when the solution is not disturbed in any way. Under this condition, the solution contains more of the solute than is ordinarily present in a saturated solution under the existing conditions; it is then called a **supersaturated solution**. If a crystal of the dissolved substance is brought into contact with a supersaturated solution, the excess of solute immediately separates from the solution.

31. Strengths of Solution.—The term strength, used in many ways in chemistry, is not sufficiently definite to be used for expressing the proportions of solvent and solute in solutions, and some other means of stating these proportions is needed.

The relative amounts of solvent and solute in a solution is generally described as the *concentration* of that solution. A *dilute solution* is a solution containing a small proportion of solute, and a *concentrated*, or *strong*, solution is a solution containing a large proportion of solute. The removal of part of the solvent is called *concentrating* and the removal of all the solvent by evaporation is described as *evaporating to dryness*.

It should be borne in mind that a saturated solution is not necessarily a concentrated solution, for, in many cases, but small amounts of substances may be needed to produce saturated solutions. Therefore, the terms pertaining to concentration are not used in connection with those applying to degree of saturation.

IONIZATION

PRINCIPLES OF ELECTROLYSIS

32. Conductors.—The disappearance of solutes in solvents to form homogeneous, clear, transparent mixtures is a phenomenon that can readily be observed, but what actually takes place within the solution needs further consideration.

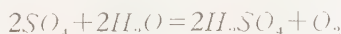
The effects of an electric current serve to bring out several facts of importance to the study of changes during solution. Electric currents may be conveyed from one location to another by electric conductors in which there is no evident simultaneous movement of the matter of which the conductor consists. For example, a copper wire may conduct an electric current without any evident movement of its constituent particles of copper. Such conductors are known as *conductors of the first class*. Then there are conductors of electric currents in which there is a simultaneous movement of the particles of the conductors. Solutions of acid, bases, and salts are examples of this type of conductors, known as *conductors of the second class*. A further study of the nature of solutions at this point is concerned chiefly with the conductors of the second class.

33. Electrolysis.—Absolutely pure sulphuric acid, H_2SO_4 , does not conduct an electric current, but if a solution of it is formed with water, it can conduct a current readily. Solutions that conduct an electric current are called **electrolytes**, though the term is often applied to the dissolved substance. For instance, though the term electrolyte applies to the solution of sulphuric acid in this particular instance, it is sometimes used to designate pure sulphuric acid also, in which case the thought is conveyed that a *solution* of sulphuric acid is an electrolyte.

The general method used in the *electrolysis*, or electrical decomposition, of a solution is illustrated in Fig. 1. Two plates or rods, *a* and *b*, made of suitable materials (metals or carbon) are connected to the source of an electric current, such as an electric generator or, as in this case, an electric cell *c*, and

dipped into the electrolyte *d*. These plates or rods are called *electrodes*. The electrode *b* connected with the negative pole of the battery is the *negative electrode*, or *cathode*, while the electrode *a* connected with the positive pole *c* is the *positive electrode*, or *anode*.

34. Sulphuric acid consists of a positive radical, H_2 , and a negative, or acid, radical, SO_4 . As two electric charges of opposite polarities attract each other, it follows that when an electric current is passed through a solution of sulphuric acid, the positive radical, H_2 , passes toward and collects at the negative electrode, or cathode, *b* and the negative, acid radical, SO_4 , passes toward the positive electrode, or anode, *a*. Matter, such as the positive radical, H_2 , or the negative radical, SO_4 , that travels with the current is called an **ion**. The ions that travel toward the cathode, as, for example, H_2 , are called **cations**, and ions that travel toward the anode, as, for example, SO_4 , are called **anions**. The hydrogen formed can be collected at the cathode; the SO_4 radical, on the other hand, reacts with the water, H_2O , present to form oxygen thus:



The oxygen formed gathers at the anode and can be collected, and the sulphuric acid formed again breaks up into ions to repeat the changes described. The chemical change that takes place when an electric current is passed through an electrolyte is called **electrolysis**. The foregoing changes in the electrolysis of a solution of sulphuric acid are the changes that take place when water is decomposed by an electric current into its components, hydrogen and oxygen.

35. Theory of Ionization.—The Swedish chemist Arrhenius first advanced a theory on solutions known as the

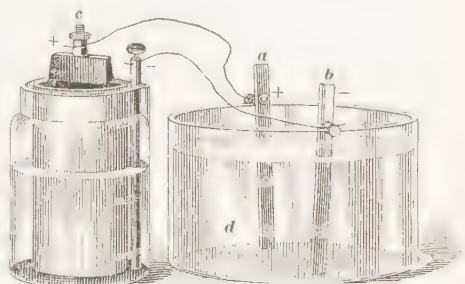


FIG. 1

theory of ionization or dissociation. Today, it forms an important part of chemical knowledge. The theory may be summarized in the following laws:

1. *The molecules of many substances, when dissolved in water, fall apart, or dissociate, into two or more parts called ions.*

2. *An ion differs from an atom or molecule in that it carries an electric charge.*

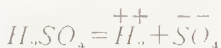
3. *Two kinds of ions are formed: one charged with positive electricity and the other with negative electricity, the sum of the positive charges being sufficient to neutralize exactly all the negative charges.*

4. *Only electrolytes dissociate into ions.*

36. The meaning of these laws may be brought out more clearly by considering the formation of a solution of common salt, sodium chloride, in water. According to the theory of ionization, some of the molecules of sodium chloride, $NaCl$, dissociate when dissolved in water into ions of sodium and chlorine. If an electric current were to be passed through this solution, it would be found that the sodium ions, which are charged with positive electricity, would pass toward the negative electrode and that the chlorine ions, which are charged with negative electricity, would pass toward the positive electrode. The electric charge carried by an ion is represented by placing either a plus (+) or a minus (−) sign above the symbol representing the ion. For instance, the dissociation of sodium chloride is shown in this way:



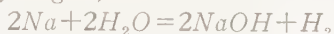
One plus or minus sign is used for each valence. The breaking up of sulphuric acid into ions would likewise be represented as follows:



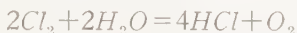
In this case, each radical is divalent and two plus and two minus signs are used.

As soon as the sodium ions come into contact with the negatively charged electrode, or cathode, they give up their positive charge and become ordinary atoms of sodium, and thereupon

they react immediately with the water present to form sodium hydroxide and hydrogen; thus:



In like manner, the ions of chlorine are attracted to the positively charged electrode, or anode, where the electric charge is given up and the ions become atoms of chlorine. These atoms either unite with other chlorine atoms to form molecules of chlorine or react with water to form hydrogen chloride and oxygen; thus:



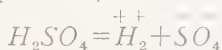
It should be borne in mind that the electric current does not cause the formation of ions, but merely directs them toward the oppositely charged electrodes. Ions are formed when the solute is dissolved in the solvent. All these laws have been verified by tests and can be accepted as facts.

There are some substances, such as sugar, that do not ionize when dissolved and these solutions do not conduct an electric current.

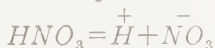
37. Ionization and Acids.—When an acid is dissolved in water, it dissociates into hydrogen ions, which always serve as cations, and into ions of the remaining radical, which always serve as anions. Hydrochloric acid dissolves in water to form cations of hydrogen and anions of chlorine; thus:



Sulphuric acid dissolves in water to form cations of hydrogen and anions of the SO_4 radical; thus:



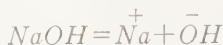
Nitric acid dissolves in water to form cations of hydrogen and anions of the radical NO_3 ; thus:



In like manner, other acids form cations of hydrogen. Hence, an **acid** may be defined as *a substance that produces hydrogen ions, when dissolved in water.*

38. Ionization and Bases.—Bases dissociate into two kinds of ions, when dissolved in water, one of which is always the hydroxyl group, OH , serving as an anion.

Sodium hydroxide, when dissolved in water, dissociates thus :



Potassium hydroxide, when dissolved in water, dissociates thus :



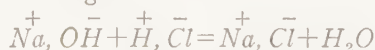
Calcium hydroxide, when dissolved in water, dissociates thus :



In like manner, other bases produce hydroxyl ions when dissolved in water. Hence, a **base** may be defined as *a substance that produces hydroxyl ions, when dissolved in water.*

39. Ionization and Salts.—Bringing together an acid and a base in proper proportions results in the disappearance of the properties of each. The resulting solution usually tastes neither sour or bitter, but is, on the contrary, salty. It has no effect on litmus, or on other indicators.

A study of the change that takes place when an acid, such as hydrochloric, is combined with the proper proportion of the base sodium hydroxide, both being in solution, shows that water is always one of the products formed. Written on the basis of ions, the change is :



The reaction shows that water is formed, and, unlike sodium and chlorine, does not remain dissociated as hydrogen and hydroxyl ions while in solution. A study of reactions of this kind has shown that hydrogen and hydroxyl ions cannot exist together in solution to any extent, but combine to form molecules of water, H_2O .

The change that forms a neutral substance, when an acid reacts with a base in the proper proportions, is called **neutralization**, and is defined as *the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water.* In like manner, a **salt** is a substance formed by the union of the anion of an acid with the cation of a base. In the foregoing example, the cation sodium of the base sodium hydroxide unites with the anion chlorine of the hydrochloric acid to form the salt sodium chloride.

40. Extent of Ionization.—It has been found that only a small fraction of the molecules in a solution ionize, depending on conditions. For instance, a dilute solution will allow a greater ionization of molecules than a concentrated solution. In other words, the greater the proportion of water (or other solvent used to form an electrolyte) the greater will be the extent of ionization.

The extent of ionization depends also on the nature of the substance dissolved. For example, at equal concentration, most salts ionize to about the same extent. Bases and acids, however, vary greatly in the degree to which they ionize when dissolved, for some are freely ionized and others but slightly.

41. Source of Electric Charges.—The thought naturally arises as to where the electric charges carried by ions are obtained. According to the modern theory, an atom consists of a minute *nucleus* of positive electricity surrounded by particles of negative electricity, called *electrons*, each having a mass equal to about one-seventeen-hundredth of that of an atom of hydrogen.

In this combination, the valences of the various elements are closely allied. An ion of chlorine, *Cl*, consists of an atom of chlorine *plus* one electron and thus has an excess of one unit negative charge; an ion of sodium, *Na*, consists of an atom of sodium *minus* one electron of sodium, and thus has an excess of one unit positive charge. When the ion of sodium unites with the ion of chlorine, the resulting product, sodium chloride, is neutral, for the excess of one unit of positive electricity in the sodium ion is neutralized by the excess of one unit of negative electricity in the chlorine ion. Hence, the atoms themselves supply the electric charges carried by ions.

42. In like manner, divalent elements when changed to ions have an excess of either two units of a positive charge or two units of a negative charge, and one ion of a divalent element or group or two ions of a univalent element or group are needed to neutralize the excess of electric units present. In other words, the valence of an element or radical designates the proportionate number of units of the electric charge carried

by an ion of that element or radical. For instance, the divalent elements, like calcium and barium, form ions $\overset{++}{Ca}$ and $\overset{++}{Ba}$ and the divalent radical SO_4 forms the ion \bar{SO}_4 .

As the study of ionization is, in itself, a broad and extensive field of study, only a brief description of the subject can be given, as far as it is applied to the ordinary chemical processes with which the pharmacist comes into contact.

THE HALOGENS: CHLORINE, BROMINE, IODINE, AND FLUORINE

43. Introduction.—The elements *chlorine*, *bromine*, *iodine*, and *fluorine* form a closely allied group of non-metals, known as the **halogens**, a term derived from the Greek, meaning *salt-producing*. The halogens are elements forming saline compounds by combining with a metal. It is to be noted that chlorine, bromine, and iodine are more closely related to one another than they are to fluorine.

CHLORINE

OCCURRENCE, PREPARATION, AND PROPERTIES

Symbol Cl. Atomic weight 35.46. Molecular weight 70.92. Valence I, III, IV, V, and VII.

44. Occurrence.—Chlorine is not found in a free state in nature, but many of its compounds, especially the chlorides of sodium, magnesium, potassium, and calcium, are abundant in the mineral world. Sodium chloride, or common salt, is found in large quantities in sea-water and in the residual deposits left where sea-water has evaporated to dryness. It is generally accompanied by the chlorides of magnesium and potassium. At Stassfurt, Germany, the strata of these residual deposits are over 1,000 feet in thickness. Some chlorides are also found in the atmosphere wherever there are bodies of salt water.

45. Laboratory Preparation.—Chlorine is easily made in the laboratory by warming manganese dioxide, MnO_2 , with concentrated hydrochloric acid, HCl . Two distinct changes enter into the process. In the first one, manganic chloride and water are formed; thus:



The manganic chloride is, however, unstable and breaks up into manganous chloride and chlorine; thus:



For reasons of economy, sodium chloride and sulphuric acid are sometimes used instead of hydrochloric acid, as they form hydrochloric acid during the preparation of chlorine; thus:



Reactions that are more complicated than others, such as this one, are determined and verified by experiment and can be accepted as true.

46. It may be noted that the change between manganese dioxide and hydrochloric acid is representative of a change that is general; that is, *when an acid reacts in the proper proportions with the oxide of a metal, the oxygen of the oxide unites with the hydrogen of the acid to form water and the metal of the oxide combines with the acid radical of the acid.* In this case, the oxygen in combination with the metal manganese unites with the hydrogen in the hydrochloric acid to form water and the metal manganese combines with the acid radical, chlorine, of the hydrochloric acid.

The best way to make chlorine in the laboratory is by treating potassium permanganate, $KMnO_4$, with concentrated hydrochloric acid that has been diluted with one-third its volume of water. The change that takes place in this case is:



An arrangement of apparatus such as is shown in Fig. 2 is used to prepare chlorine by the method described. In this method, which has been found to give satisfactory results, 10 grammes of manganese dioxide, 22 grammes of sodium chloride, and 40 cubic centimeters of sulphuric acid (made by

adding slowly and with stirring 12 cubic centimeters of concentrated sulphuric acid to 28 cubic centimeters of water) are placed in the flask *a*. The cork, holding the separatory funnel *f* (which is kept closed) and the delivery tube *c*, is placed in the neck of the flask. A wash-bottle *d*, containing water, removes any hydrochloric acid that may pass over with the chlorine. A wash-bottle *e*, containing sulphuric acid, dries the chlorine, which is then carried to a collecting cylinder *g*. A cardboard cover *h* is placed over the cylinder to prevent the escape of

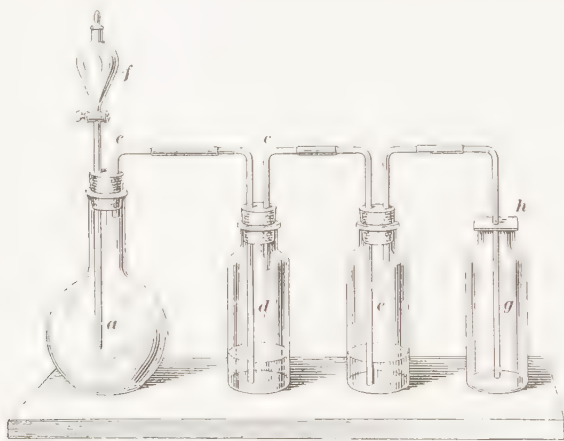


FIG. 2

chlorine into the air. Gentle heat is applied to the flask to accelerate the formation of chlorine.

CAUTION.—Care must be taken to avoid the escape of chlorine. Windows should be open when preparing this gas so as to get proper ventilation. *To inhale chlorine, in quantity, is dangerous, for it produces an inflammation of the lungs and throat.*

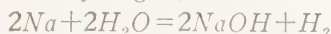
47. Commercial Preparation.—Of the many methods formerly used to manufacture chlorine, all have been or are being replaced by electro-chemical methods.

There are two ways of making chlorine electrolytically: (a) *By electrolyzing fused sodium chloride* and (b) *by dissociating sodium chloride in an aqueous solution.*

(a) *Electrolyzing Fused Sodium Chloride.*—Sodium chloride melts at 804° C. and is at this temperature a good con-

ductor of electricity. When an electric current of sufficient voltage is passed through the fused salt, gaseous chlorine is liberated at the anode and liquid metallic sodium at the cathode. The sodium, being lighter than sodium chloride, floats up through the fused material and is then converted to *sodium hydroxide*, NaOH , also called *caustic soda*. The chlorine is drawn off into collecting compartments by suction.

(b) *Electrolysis of an Aqueous Sodium Chloride Solution.* When an electric current is passed through a solution of sodium chloride (common salt) in water, chlorine collects at the anode and sodium at the cathode. The reactions taking place during this electrolysis are complicated. Most of the chlorine is collected, but a small portion dissolves in the electrolyte and begins to diffuse toward the cathode. The sodium liberated at the cathode immediately combines with water to form caustic soda and hydrogen; thus:



The caustic soda at once begins to diffuse toward the anode. When chlorine diffusing toward the cathode meets the caustic soda diffusing toward the anode, sodium hypochlorite, NaClO , sodium chloride, and water are formed; thus:



The reactions are still more complicated when both the caustic soda and sodium hypochlorite react further. However, chlorine, caustic soda, and hydrogen are the final products obtained.

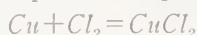
48. Physical Properties of Chlorine.—Chlorine is a greenish-yellow gas, having a peculiar, suffocating odor. Inhaled in small amounts it irritates the throat and lungs, and inhaled in larger amounts it produces serious effects. Some relief from these effects can be obtained by inhaling ether or ammonia.

It is about two and one-half times as heavy as air. One volume of water at 20°C . dissolves over 2 volumes of the gas. Owing to its solubility, it is generally collected by downward displacement of air, though it can be collected above a strong salt solution, in which the gas is not readily soluble.

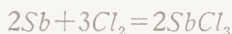
Chlorine can be liquefied by compression at ordinary temperatures to a yellow liquid, and is supplied for commercial use in this form in steel cylinders. This liquid cooled below -102° C. changes to a pale-yellow solid.

49. Chemical Properties of Chlorine.—Chlorine is chemically one of the most active of all elements, for it unites directly with many elements and can replace many others in compounds.

It unites with metals with great readiness. If copper, in the form of thin strips, is placed in chlorine, it reacts with evolution of light and heat to produce cupric chloride; thus:

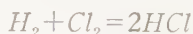


Antimony in powdered form unites with chlorine to produce antimony chloride; thus:

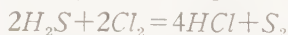


In like manner, all the common metals, excepting gold and platinum, unite with chlorine to form chlorides.

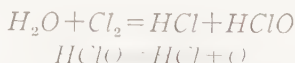
50. Chlorine exhibits an especially strong chemical affinity for hydrogen, both free and combined. If a jet of hydrogen burning in air is inserted into chlorine, it will continue to burn, forming hydrogen chloride; thus:



It can also displace elements that are combined with hydrogen, as, for example, in hydrogen sulphide; thus:



It reacts with the stable substance hydrogen monoxide, or water, with the liberation of oxygen, by first forming hypochlorous acid, which in turn can decompose to form hydrogen chloride and oxygen; thus:



As the oxygen liberated from this combination can oxidize organic coloring matter to colorless products, moist chlorine is frequently used as a bleaching agent.

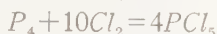
Chlorine unites with non-metallic elements also. Sulphur, when heated in the presence of chlorine, forms sulphur monochloride, S_2Cl_2 ; thus:



It reacts with phosphorus to form either phosphorus trichloride; thus:



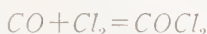
Or, phosphorus pentachloride; thus:



depending on the amount of chlorine present.

Chlorine does not unite directly with carbon, nitrogen, or oxygen, but can do so indirectly.

Chlorine unites directly with carbon monoxide in the sunlight to form carbonyl chloride, a liquid volatile at 8.2° C., commonly called *phosgene*; thus:



51. Uses of Chlorine.—Dry chlorine will not bleach dry colored cloth, but if the cloth is wet and then brought in contact with chlorine, the coloring matter in the cloth is oxidized to colorless products, in which case the cloth is said to have been *bleached*. This action is due to the formation of hypochlorous acid, which liberates oxygen. Bleaching by means of chlorine is resorted to in many industries. As fabrics from vegetable fibers, such as straw, flax, and cotton, are in their natural colors slightly yellow, chlorine bleaching is often applied to turn them white. Likewise, foods, such as dried fruits and flour, are bleached by this process.

Chlorine, both in the free state and in compounds from which it is readily liberated, is also used as a *disinfectant*; that is, a material that destroys bacterial growth.

COMPOUNDS OF CHLORINE

HYDROGEN CHLORIDE

52. Occurrence of Hydrogen Chloride.—A solution of the gas hydrogen chloride, known as **hydrochloric**, or **muriatic acid**, is one of the principal chemicals used in laboratory work. The gas does not occur to any extent in nature, though some small quantities are found in volcanic gases and in some natural waters. The gas or its solution must be made from naturally occurring chlorides by treating them with acid.

53. Laboratory Preparation.—While hydrogen chloride can be prepared by burning hydrogen in an atmosphere of chlorine, as has already been stated, this method of preparation is not nearly as convenient or satisfactory as the one in which sodium chloride is acted on by sulphuric acid. If the reaction takes place at ordinary temperature, the following change occurs:



This equation shows that 1 molecule of sodium chloride reacts with 1 molecule of sulphuric acid to produce 1 molecule of sodium hydrogen sulphate, also called *acid sodium sulphate*, or *sodium bisulphate*, and 1 molecule of hydrogen chloride. If a much higher temperature is used, the sodium hydrogen sulphate can react with more sodium chloride to form more hydrogen chloride; thus:



or, combining the two changes that occur at the higher temperatures,



In this preparation, 15 grammes of dry salt are placed in the flask *a*, Fig. 3, and 25 cubic centimeters of sulphuric acid is poured down through the thistle tube *c*. The flask is then warmed gently. The hydrogen chloride is rapidly given off and is collected by displacement of air in the cylinder *b*. A

solution of hydrogen chloride, hydrochloric acid, can be made by passing the hydrogen chloride through a delivery tube *d* that just extends to the surface of the water *e* in the cylinder *b*. Owing to its great solubility in water, the gas readily dissolves in the water. (U. S. P., pages 13 and 14.)

54. Commercial Manufacture of Hydrochloric Acid.—Hydrochloric acid is one of the products made in the

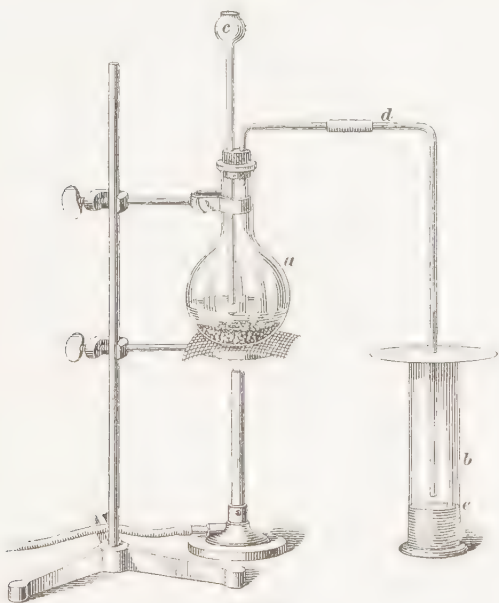
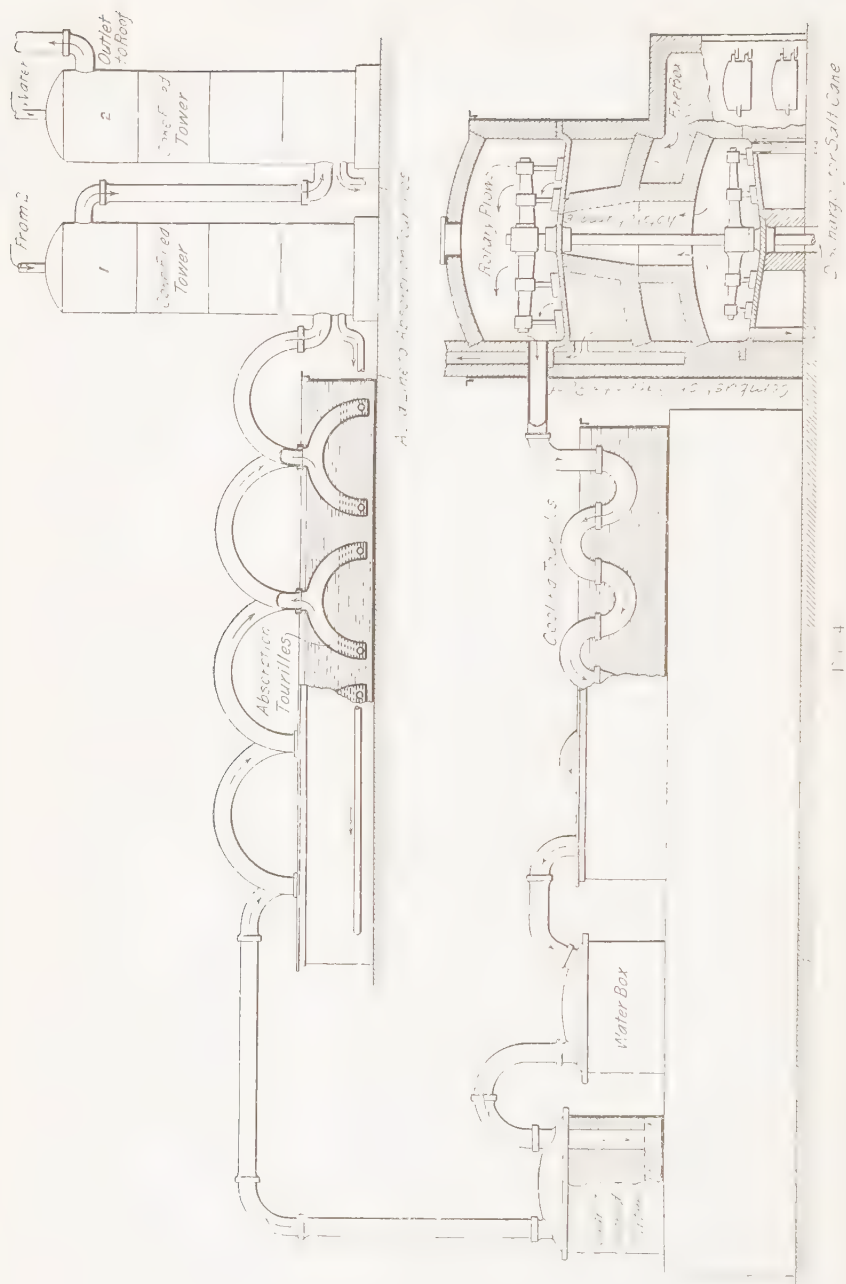


FIG. 3

manufacture of sodium sulphate, known as *salt cake*. The reactions are the same as those shown in the laboratory preparation.

Niter cake, a by-product made in the manufacture of nitric acid, contains impure sodium bisulphate and about 32 per cent. of free sulphuric acid. This material is now being used instead of pure sulphuric acid to react with sodium chloride to form hydrogen chloride. This is a good example of the application of a material to a manufacturing process that would otherwise be a waste product.



The niter cake and salt are crushed and mixed in proper proportion, which depends on conditions. The mixture is then fed into the top of a furnace, as shown in Fig. 4, the temperature of which is about 215° C. At this stage, the sulphuric acid in the niter cake reacts with the salt to produce hydrogen chloride. The residue, salt cake, is removed for use in the manufacture of glass, etc.

The hydrogen chloride rises to the top of the furnace and enters a series of stoneware U tubes and a water box where the gas is cooled. The hydrogen chloride next passes through a quartz filter, where its mechanically carried impurities are removed. It next enters a series of absorption arrangements, called *tourilles*, containing dilute hydrochloric acid, where the gas dissolves to form a strong solution of the gas in water. Gas that is not dissolved at this point passes up through absorption towers filled with coke for retarding the passage of the gas so that the maximum amount will be absorbed by water passing down through the towers. The solution of acid flowing back from the towers passes back into the absorption *tourilles*, where it absorbs more hydrogen chloride to form concentrated hydrochloric acid.

55. Physical Properties of Hydrogen Chloride.

Hydrogen chloride is a colorless gas having a suffocating, irritating effect when inhaled. It is one-fourth heavier than air and is extremely soluble in water. Under ordinary conditions of temperature and pressure, 1 volume of water dissolves nearly 500 volumes of the gas. If such a solution is heated, the gas passes off until, at boiling point, 110° C., but 20.2 per cent. by weight of hydrogen chloride is left in the solution. Continued boiling does not alter the percentage of gas in solution.

Hydrogen chloride fumes brought in contact with moist air form a solution of hydrogen chloride. It neither burns nor supports combustion.

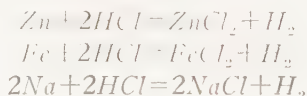
56. Chemical Properties of Hydrogen Chloride.

Hydrogen chloride is chemically rather inert and stable. This gas has no action on non-metals, such as carbon and sulphur,

but does react with some of the more active metals, such as potassium, sodium, and magnesium, to form chlorides of these metals with the liberation of hydrogen. It combines directly with ammonia gas, NH_3 , to form a dense cloud of ammonium chloride, NH_4Cl .

Hydrochloric acid, the solution of hydrogen chloride in water, exhibits marked chemical properties. It is a strong acid, turning blue litmus red, reacting with metals to liberate hydrogen and to form chlorides of the respective metals, and with oxides and hydroxides of metals (bases) to form chlorides of the metals and water. Following are some chemical equations showing these changes:

With metals, hydrochloric acid forms:



With bases, hydrochloric acid forms:



57. Aqua Regia.—Many oxidizing agents decompose hydrochloric acid. One of them, *nitric acid*, HNO_3 , reacts with it to form chlorine, nitrosyl chloride, and water; thus:



A mixture of concentrated hydrochloric and concentrated nitric acids contains, therefore, several oxidizing agents and because it dissolves the so-called noble metals, gold and platinum, it is called **aqua regia** which means "royal water."

58. Chlorides.—Most chlorides are soluble in water. The common exceptions are: The *mercurous chloride*, $HgCl$; *silver chloride*, $AgCl$; and *lead chloride*, $PbCl_2$. Less common exceptions are: *Cuprous chloride*, $CuCl$; *aurous chloride*, $AuCl$; and *thallous chloride*, $TlCl$. This fact is the basis for many manipulations and tests performed by the analytical chemist.

59. Uses for Hydrochloric Acid. Hydrochloric acid has a wide range of industrial uses and is lending itself yearly

to new ones. One of its chief applications is in the process of removing scale and rust from a metal to cleanse it before coating it with tin. This cleansing process is called *pickling*. It is also used in the manufacture of bleaches, glue, and gelatine, and in the reduction of tungsten ores. Its uses in the laboratory are varied and numerous.

OXIDES AND OXYACIDS

60. Oxides and Oxyacids of Chlorine.—In addition to hydrochloric acid, there are other acids containing chlorine, hydrogen, and oxygen, which vary in the amounts of oxygen present. Following is a list of the names and formulas of the substances:

OXIDES	ACIDS
Hypochlorous anhydride, Cl_2O	Hypochlorous, $HClO$
Chlorine dioxide, ClO_2	Chlorous, $HClO_2$
Perchloric anhydride, Cl_2O_7	Chloric, $HClO_3$
	Perchloric, $HClO_4$

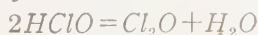
POTASSIUM SALTS

Potassium hypochlorite, $KClO$
 Potassium chlorite, $KClO_2$
 Potassium chlorate, $KClO_3$
 Potassium perchlorate, $KClO_4$

61. Nomenclature.—In connection with the preceding names and formulas, it should be noted that the suffixes *ic* and *ous* indicate more and less oxygen, respectively; the prefix *hypo* means still less and *per* still more oxygen. These suffixes and prefixes are relative terms used within this particular group; their meanings will also be the same when used for other acid groups, such as H_2SO_4 and H_3PO_4 , so far as they apply to the oxygen contents of the different acids which make up the group.

62. Hypochlorous Acid.—Hypochlorous acid is an unstable acid and can be kept only in dilute solutions. In strong solutions or under the influence of heat it decomposes in one of the following three ways:

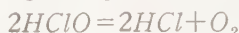
1. It can break up into chlorine monoxide, Cl_2O , known also as *hypochlorous anhydride*, and water; thus:



2. It can decompose into chloric acid and hydrochloric acid; thus:



3. Exposed to sunlight, it gives off oxygen; thus:

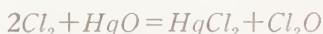


63. Laboratory Preparation of Hypochlorous Acid.

A solution of hypochlorous acid can be made in the laboratory by dissolving chlorine monoxide in water, as shown in the equation:



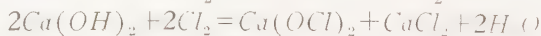
The chlorine monoxide is made by passing chlorine gas over freshly precipitated mercuric oxide, HgO . The mercuric oxide is made by adding a solution of sodium hydroxide to a solution of mercuric nitrate, filtering off the precipitate and drying it at about $350^\circ C$. The action between chlorine and mercuric oxide is:



64. Commercial Manufacture of Hypochlorites.

In commerce, neither hypochlorous acid nor its pure salts are made, for the impure hypochlorites can be more cheaply manufactured and serve as well in industrial operations.

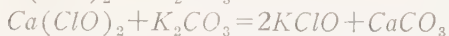
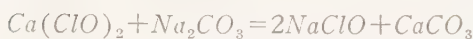
Chlorine unites with the hydrate of sodium, potassium, or calcium in the presence of moisture to form the corresponding hypochlorite, as shown in these reactions:



The chlorides present with the hypochlorites do not interfere with the action of the latter and no effort is, therefore, made to separate them.

Aqueous solutions of hypochlorites are produced in large quantities for immediate use at the place of manufacture, but owing to the bulk of the hypochlorite solutions and their instability, they are not generally transported.

The hypochlorites of sodium or potassium can be made by treating calcium hypochlorite with the carbonate of sodium or potassium, respectively, as shown in these reactions:

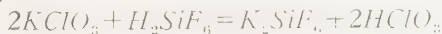


65. In many cases calcium hypochlorite is used, which is cheaper than either sodium hypochlorite or potassium hypochlorite, and which meets the same requirements as either of these salts for many purposes. It is manufactured in large quantities by absorbing chlorine in a suspension of hydrated lime, $Ca(OH)_2$, in water, called *milk of lime*. In this process, the temperature must be kept below 35° C. and an excess of lime must always be present, or the hypochlorite will begin to decompose with the formation of calcium chlorate. In the manufacture of this solution of calcium hypochlorite, called also *bleach liquor*, the chlorine gas is generally mixed with air before it is passed into the suspension of lime so as to prevent overheating.

66. In another process for the manufacture of bleaching powder, burnt lime that is low in magnesium oxide and free from carbon dioxide is spread in a layer about 3 inches deep in a chamber having a floor of asphalt and sides of lead, stone, or cement. This chamber is connected to a series of similar chambers, the floors of which are also covered with lime. A mixture containing about 40 per cent. of chlorine and 2 per cent. of air is admitted through the roof of the first chamber. It passes slowly over the lime in this chamber and is partially absorbed, then passes into the second chamber, where it is further absorbed, and so on until it is practically all absorbed. As soon as the lime has absorbed all the chlorine it can, it is placed either in wooden casks or in iron drums for shipment. (U. S. P., pages 90 and 96.)

Bleaching powder, known also as **chloride of lime**, is the most convenient and economical kind of bleaching material as far as portability is concerned.

67. Chloric Acid.—The addition of hydrofluosilicic acid to a solution of potassium chlorate results in the formation of chloric acid; thus:



The insoluble potassium fluosilicate is removed by filtration.

The solution of chloric acid can be concentrated to about 40 per cent., but must not be heated above 40° C., for it then decomposes to yield chlorine dioxide and perchloric acid; thus:



The concentrated solution of chloric acid is a thick, colorless, liquid. It readily gives up oxygen, even setting fire to paper that has been dipped in it.

68. Chlorates.—Of the salts of chloric acid, the one called **potassium chlorate** is the best known and most abundantly used. It can be made by passing an excess of chlorine into a warm, concentrated solution of potassium hydroxide, as shown in this reaction:

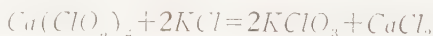


But as in this process 5 molecules of potassium chloride are made for each molecule of potassium chlorate, a more economical way of making potassium chlorate is used, based on the fact that calcium chloride is cheaper than potassium chloride.

In the latter process, calcium hydroxide, as milk of lime, instead of potassium hydroxide, serves as the raw material. Chlorine, in excess, is passed over milk of lime, in cast-iron cylinders provided with stirrers, until most of the calcium hydroxide has been acted on by the gas. The chlorine that is not taken up by calcium hydroxide in the first cylinder passes on into a second one where more calcium hydroxide is acted on. In this change, calcium chlorate and calcium chloride are formed, as shown by the reaction:



Potassium chloride is then added to the solution of calcium chloride and calcium chlorate, whereupon calcium chlorate is changed to potassium chlorate; thus:



Water is evaporated off until the solution has a specific gravity of 1.35. When the solution is cooled, potassium chlorate crystals, being less soluble than those of calcium chloride, separate out. The liquor left after the potassium chlorate has been removed is concentrated by evaporating off part of its

water a second and a third time; then the solution is cooled, to recover the small amount of potassium chlorate left. The crude potassium chlorate is purified by redissolving it in water and by recrystallizing it again by concentrating and cooling.

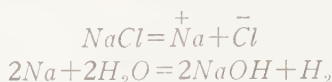
69. As **sodium chlorate** is more readily soluble than potassium chlorate, the method of making it is somewhat different from that used in making the potassium salt. Calcium chlorate is made in the same way and sodium chloride is then added to the solution. The mixture is next boiled down until it is of a specific gravity of 1.50 and, then, cooled. About four-fifths of the calcium chloride (being less soluble than sodium chlorate) crystallizes from the solution. The remaining liquor is drained off and most of the calcium salt is precipitated as calcium sulphate by the addition of sodium sulphate; thus:



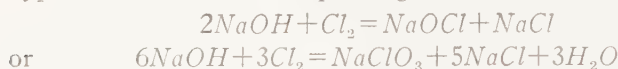
The solution of sodium chloride and sodium chlorate is separated from the precipitate of calcium sulphate and is boiled down. Most of the sodium chloride separates from the boiling solution and is removed. The solution is then cooled and most of the sodium chlorate, which crystallizes out, is recovered.

70. Fractional Crystallization.—The manufacture of *potassium* and *sodium chlorates* brings out a method of separating two soluble products. Both potassium chlorate and calcium chloride are soluble, but the former is less soluble than the latter. If the solution is concentrated, that is, if the amount of solvent present is reduced, and the temperature of the solvent is lowered, less substance can remain in solution. A point is finally reached where the solvent cannot hold in solution all of the dissolved materials, and a part of it must separate from the solution. In such cases, the less soluble material separates first. The process whereby soluble substances are separated from one another by crystallizing out the least soluble substance first, and then the others present in order of their solubilities, is known as **fractional crystallization**. It is the crystallization of a substance from a solution, in fractions, each of which is more soluble than the fraction previously removed.

71. Electrolytic Manufacture of Hypochlorite and Chlorate.—The electrolysis of an “alkali chloride” solution results in the formation of the alkali and chlorine; thus:



If the electrolytic cell is so constructed that the chlorine and sodium hydroxide are brought into contact, a condition exists that permits of the manufacture of either the chlorate or the hypochlorite of sodium, depending on the conditions; thus:



Above 40° C. and with the solution slightly acid, the *chlorate* is made; below 40° C. and with the solution less acid, *hypochlorite* is produced. In practice, a temperature of 70° to 100° C. is maintained in the production of chlorate.

72. Uses of Chlorates.—Chlorates are the chief sources for oxygen in the laboratory, and are extensively used in industrial work where a substance that yields oxygen readily is needed, as in fireworks, matches, and explosives.

73. Perchloric Acid.—Perchloric acid is made by distilling a mixture of potassium perchlorate and concentrated sulphuric acid very carefully under a pressure of 56 millimeters, the reaction being:



Perchloric acid is a colorless liquid that decomposes very readily, but can be kept satisfactorily in a 70 per cent. solution. It is an active oxidizing agent, and when heated above 92° C., it explodes. Under a pressure of 56 millimeters, it boils at 39° C.

74. Potassium Perchlorate.—Potassium perchlorate, one of the principal salts of perchloric acid, is made by heating potassium chlorate cautiously, the reaction taking place being as follows:



Potassium perchlorate can be separated from potassium chloride by grinding the mixture with a very small amount of

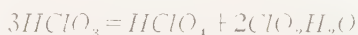
water, whereupon the more soluble potassium chloride dissolves and leaves the potassium perchlorate undissolved.

Perchlorates, though less readily decomposed than chlorates, are also used as materials that yield oxygen readily, especially in the manufacture of fireworks and matches.

75. Oxides of Chlorine.—There are three oxides of chlorine: (a) Hypochlorous anhydride, or chlorine monoxide, Cl_2O ; (b) chlorine dioxide, ClO_2 ; and (c) perchloric anhydride, Cl_2O_7 . None of these can be made by the direct chemical combination of oxygen and chlorine.

(a) *Chlorine Monoxide*.—As already explained, chlorine monoxide is made by passing chlorine over properly prepared mercuric oxide.

(b) *Chlorine Dioxide*.—Chlorine dioxide is produced when chloric acid is warmed above $40^\circ C$., thus



It is a yellow gas which can be liquefied. The liquid boils at $10^\circ C$. Mixed with water, the oxide forms a mixture of chlorous and chloric acids.

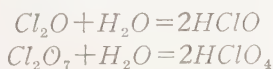
(c) *Perchloric Anhydride*.—Perchloric anhydride is made by adding phosphorus pentoxide to perchloric acid at a very low temperature, in which case the following change occurs:



The perchloric anhydride is separated from the metaphosphoric acid by gentle distillation.

Perchloric anhydride is a colorless liquid which explodes when struck or strongly heated. It boils at $82^\circ C$. under normal pressure.

76. Anhydrides.—*Hypochlorous anhydride* and *perchloric anhydride* are called anhydrides because they form hypochlorous acid and perchloric acid, respectively, when combined with water, thus:



The term *anhydride* is applied to oxides that form acids when combined with water. The number of molecules of water

combining with 1 of the oxide will vary with the different materials. The name of the anhydride is taken from the acid formed. For example, SO_3 is called, not only *sulphur trioxide*, but also *sulphuric anhydride*, because, combined with water, it forms sulphuric acid as shown in the equation :



Likewise, N_2O_5 , *nitrogen pentoxide*, is also called *nitric anhydride*, because it combines with water to form nitric acid, thus :



BROMINE

OCCURRENCE, PREPARATION, AND PROPERTIES

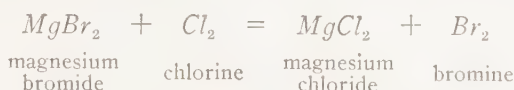
Symbol Br. Atomic weight 79.92. Molecular weight 159.84. Valence I and V.

77. History.—Bromine was discovered by Balard in 1826, in the examination of *bittern*, which is the liquid remaining after the sodium chloride and some other salts have been made to crystallize by evaporating sea-water, which contains only about 1 grain of bromine per gallon in the forms of bromide of magnesium and bromide of sodium. Owing to its disagreeable odor, he gave it the name bromine, which is derived from the Greek word for stench.

78. Occurrence.—Like chlorine, this element is never found uncombined in nature, but always in combination with other elements, such as sodium, potassium, and magnesium. It occurs in the waters of the springs of Kreuznach and Kissingen, in Germany, and also has been obtained from various saline springs in the United States and from the mother liquors of the salt works at Stassfurt, in Germany.

79. Preparation.—The first step in the preparation of bromine is to separate the bromides from the chlorides with which they are associated. The solid salts are dissolved, and

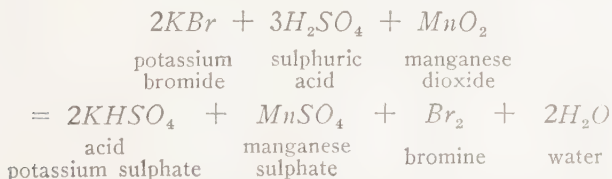
then concentrated by evaporation; the chlorides, being less soluble, first crystallize out and leave a mother liquor, or bittern, in which the bromides predominate. There are two reactions by which bromine may be obtained from this liquid. If chlorine is passed through the solution, bromine is liberated according to the equation:



The bromine at first set free imparts a reddish-brown color to the solution. On shaking this with ether the bromine is dissolved, and its ethereal solution rises to the surface, and may be poured from the watery layer underneath. On this ethereal solution being treated with potassium hydrate, its red color disappears, bromide and bromate of potassium being formed:



The ether may be distilled off and recollected; the solid residue of bromide and bromate is ignited in order to decompose the bromate, which splits up into bromide and oxygen in the same manner as does potassium chlorate. In this way potassium bromide is obtained; the bromine may again be liberated by gently heating the bromide with manganese dioxide and sulphuric acid, when a reaction occurs analogous to that which takes place when a chloride is similarly heated:



At times, the mother liquor, instead of being treated with chlorine, is evaporated to dryness and the residue mixed directly with sulphuric acid and manganese dioxide; but, in this case, as chlorides are always present in greater or less quantity, the bromine is liable to be contaminated with chlorine.

80. Properties.—Bromine, at ordinary temperatures, is a dark, brownish-red liquid, so heavy that glass floats readily in it; it possesses an exceedingly penetrating and disagreeable odor, somewhat recalling that of chlorine. At a temperature of 58.7°C ., it boils and is converted into a deep-red vapor that is about five and one-half times more dense than air. Bromine freezes at -7.2°C ., forming a dark-brown mass of delicate needles, with a metallic luster. Water dissolves bromine but slightly, 33 parts of it dissolving, at a temperature of 15°C ., only 1 part of bromine. This solution possesses bleaching powers, but not to such an extent as chlorine. In this, as in other reactions, bromine and chlorine closely resemble each other, but bromine is the less active of the two, and is displaced from its compounds by chlorine. It is an active corrosive poison.

Bromine colors starch yellow, and a bromide in aqueous solution precipitates silver from its solutions as yellow silver bromide. Bromine and its salts are used principally in photography and in medicine. (U. S. P., page 527.)

IODINE

OCCURRENCE, PREPARATION, AND PROPERTIES

Symbol I. Atomic weight 126.92. Molecular weight 253.84. Valence I, V, and VII.

81. History and Occurrence.—Iodine, as well as bromine and chlorine, is found in sea-water, but in considerably smaller quantities. Sodium iodide, NaI , appears to constitute a portion of the necessary food of certain varieties of seaweed, which extract it from the sea-water and concentrate it in their tissues. On the coasts of Scotland and Normandy large masses of seaweed were formerly burned in order to extract the soda that they contained. The ash remaining, called *kelp*, or *varec*, was dissolved in water, and the soda salts crystallized out. In the year 1811, Curtois, a soap manufacturer of Paris, being

engaged in the manufacture of soda from kelp, obtained from the waste liquors a substance that possessed properties different from those of any matter with which he was acquainted. He turned this substance over to Clement, a French chemist, who satisfied himself that it was an entirely new, and, so far, unknown substance. Davy and Gay-Lussac, in 1813, determined the elementary character of this substance, and named it iodine, derived from a Greek word, in allusion to the beautiful violet color of its vapor.

82. Preparation.—Iodine is prepared from its salts in the same manner as is chlorine and bromine, by the treatment of the iodides with manganese dioxide and sulphuric acid:



Upon heating the mixture thus obtained, the iodine vapor passes over and is condensed.

In later years the largest amount of iodine is obtained from the mother liquors of crude Chile saltpeter, $NaNO_3$. These liquors contain the iodine in the form of sodium iodate and iodide. The liquors are treated with sodium bisulphite, the iodine separates out in a solid form, is filtered off, and purified by sublimation. The commercial product thus obtained is washed with a little water, dried on porous plates, and resublimed.

83. Properties.—The properties of iodine are well marked; at ordinary temperatures it is a dark-colored (bluish-black) solid, possesses a metallic luster, and gives off small quantities of vapor of a violet tint. It melts at 115° C. and boils at 184.35° C., evolving a dense, violet, nearly black-appearing vapor that is 8.72 times heavier than air, and is the heaviest vapor known; at $1,700^\circ$ C., however, the density of this vapor is reduced about one-half. The vapor possesses an odor resembling that of chlorine, which may even be noticed on smelling the substance at ordinary temperatures. Iodine is only very slightly soluble in water, to which it imparts a light yellowish-brown tint, 1 part of iodine requiring about 7,000 parts of water. It dissolves in carbon disulphide and chloroform, to which it imparts a violet tint, resembling the color of

its vapor, as well as in alcohol and ether; the two last-named substances form with this element a brown solution. In chemical reaction iodine closely resembles chlorine and bromine, though it is less active than these two elements. It bleaches but faintly, if at all, in full sunlight, but combines directly with all metals to form iodides. Being less active than chlorine and bromine, it may be liberated from the iodides by the addition of either chlorine or bromine. On the other hand, the oxygen compounds of iodine are far more stable than those of chlorine and bromine.

Starch is the characteristic reagent for free iodine. It forms with it a deep-blue color, which is so intense that 1 part of iodine may be detected by it in 300,000 parts of water; this blue color vanishes on boiling, but reappears as the liquid cools. Iodine does not give this reaction when in a state of combination. The most delicate test for iodine is the purple-red color it produces when dissolved in carbon disulphide, CS_2 ; 1 part of iodine in 1,000,000 parts of water may be detected in this way. Iodine stains the skin yellow, but is not an active poison.

84. Uses.—Iodine, both free and in combination, has found an extended use in the manufacture of aniline colors and in medicine, being particularly serviceable in glandular affections. *Tincture of Iodine*, U. S. P., is known as “drug store” iodine. It is a solution of potassium iodide and iodine in a mixture of alcohol and water. Iodine salts are also used extensively in photography. (U. S. P., pages 228, 229, 247, 481, 535.)

FLUORINE

OCCURRENCE, PREPARATION, AND PROPERTIES

Symbol F. Atomic weight 19.0. Molecular weight 38.0. Valence I.

85. Occurrence and History.—Fluorine occurs widely distributed in nature, but always in combination with other elements. It is found most frequently crystallized in cubes

and octahedra, as the fluoride of calcium, CaF_2 , under the name of *fluorspar*. It also occurs as *cryolite*, a fluoride of aluminum and sodium, $3\text{NaF} + \text{AlF}_3$. It has also been detected in minute quantities in sea-water and in the water of many mineral springs. Fluorine has also been found in the enamel of the teeth, the bones of mammals, in the blood, the brains, and in milk. It is used in the form of fluorspar (from *fluo*, I flow) as a flux and derives its name from the property this compound has of melting when heated. Owing to its remarkable affinity for other elements, fluorine has resisted until recently all attempts to isolate it.

86. Preparation and Properties.—Hydrofluoric acid is obtained from fluorspar, which is a compound of fluorine with calcium, CaF_2 , by the action of sulphuric acid. The element is nearly colorless and possesses the properties of chlorine, but much more strongly developed, and has an odor resembling that of hypochlorous acid. It unites directly with hydrogen even without the aid of light, and decomposes water readily. Sulphur, selenium, phosphorus, iodine, arsenic, antimony, silicon, boron, potassium, and sodium take fire in it spontaneously. Potassium chloride and potassium iodide are readily decomposed by fluorine, which liberates the chlorine and iodine. Organic substances are violently attacked and inflamed in it. It liquefies at -187°C ., with the aid of boiling oxygen. In the *liquid* form it loses, almost completely, its chemical properties. It unites readily, however, with hydrogen, but does not attack glass, iodine, sulphur, or metals.

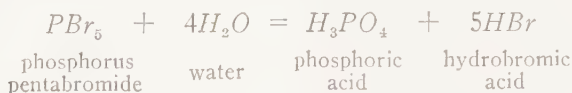
By igniting platinum fluoride, Moissan has obtained fluorine in an exceptionally pure form.

HYDROGEN COMPOUNDS OF BROMINE, IODINE, AND FLUORINE

87. Hydrobromic Acid, HBr .—The most instructive method of preparing hydrobromic acid consists in attacking phosphorus by bromine in the presence of water, when phosphorus pentabromide is formed according to the equation:

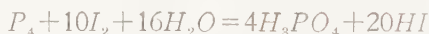


This is decomposed by the water as fast as it is formed, yielding phosphoric and hydrobromic acids:



Hydrobromic acid is very similar to hydrochloric acid; it is a colorless acid gas, fuming strongly in moist air, and is very soluble in water. It liquefies at -68.7°C. , and the liquid freezes at a temperature of -86.13°C. It dissolves readily in water, forming a solution having a specific gravity of 1.78 and containing 82 per cent. hydrobromic-acid gas. (U. S. P., page 12.)

88. Hydriodic Acid, HI.—Hydriodic acid is prepared by acting on phosphorus with iodine in the presence of water, when reactions take place that are analogous to those occurring when hydrobromic acid is prepared in the same way and may be expressed in the equation:

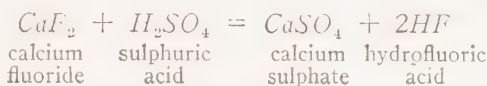


The hydriodic acid prepared in this way almost always contains some phosphorus compounds.

89. Hydriodic acid, like hydrobromic acid, is a colorless gas, with a specific gravity of 4.41; it has an acid reaction, and fumes in the air. It easily condenses to a liquid by a pressure of 4 atmospheres at 0° ; the liquid thus obtained, when cooled to -55°C. , freezes to a clear, ice-like solid which melts at -51.3°C. It is soluble in water, like hydrochloric acid, yielding at 0° a solution of specific gravity 1.99. It is less stable than hydrobromic acid, as it gives up its hydrogen more readily; consequently, it cannot be prepared by acting on an iodide with sulphuric acid, for the hydriodic acid is decomposed as fast as formed, depositing free iodine.

If allowed to stand, the solution of hydriodic acid in water soon begins to decompose. The oxygen of the air combines with the hydrogen, forming water and setting free the iodine, which gives the solution a brown color. (U. S. P., pages 11 and 427.)

90. Hydrofluoric Acid, HF .—Hydrofluoric acid is the most important compound of fluorine, and is prepared either by the action of sulphuric acid on calcium fluoride, calcium sulphate and hydrofluoric acid resulting, according to the equation:



or by heating dry acid potassium fluoride, KHF_2 , to redness in a platinum still. The hydrofluoric acid thus obtained is a colorless liquid that boils at 19.4°C ., and has a specific gravity of .985 at 12° ; it solidifies at -102° and melts at -92° . It has a most pungent, irritating odor, which, when inhaled in even small quantities, causes serious irritation of the lungs. The acid corrodes the skin when brought in contact with it and creates painful ulcers.

Hydrofluoric acid dissolves all metals except lead, gold, and platinum, and has only a slight action on magnesium. It dissolves sodium and potassium as does water. It decomposes the oxides of silicon and boron. When perfectly dry it has no action on glass, but the slightest trace of moisture causes it to decompose glass, the silica contained being dissolved, according to the reaction:



Hydrofluoric acid decomposes metallic silicates, forming a metallic fluoride, which is in turn decomposed by either sulphuric or hydrochloric acid.

OXIDES AND ACIDS OF BROMINE AND IODINE

91. The compounds of bromine and iodine with oxygen and hydrogen are very similar to the corresponding compounds of chlorine. The compounds formed by bromine are *hypobromous acid*, HBrO ; *bromic acid*, HBrO_3 ; and possibly *perbromic acid*, HBrO_4 . The compounds formed by iodine are *iodine pentoxide*, I_2O_5 ; *iodic acid*, HIO_3 ; *periodic acid*, HIO_4 .

92. Hypobromous Acid, HBrO .—It has not been possible to prepare hypobromous acid in a pure state because of

its instability. Its salts are prepared by a method similar to that used for the preparation of the hypochlorites. Bromine acting on a dilute solution of potassium hydrate produces potassium hypobromite according to the equation:



Bromine vapor acting on calcium hydrate (slaked lime) forms a compound similar to bleaching powder.

93. Bromic Acid, $HBrO_3$.—Bromic acid has not been obtained in a pure state, but its salts are prepared in the same manner as the chlorates. By treating a concentrated solution of potassium hydrate with bromine, potassium bromate is obtained according to the equation:

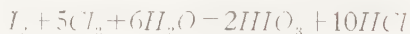


In chemical behavior the bromates resemble the chlorates.

94. Perbromic Acid, $HBrO_4$.—There is considerable doubt in regard to the existence of perbromic acid. One investigator claims to have obtained it as an oily, colorless liquid by decomposing perchloric acid with bromine, but others have failed to get it by this or any other method.

95. Iodine Pentoxide, I_2O_5 .—Iodine pentoxide is a white solid that is obtained by heating iodic acid to $170^\circ C$. It dissolves readily in water, forming iodic acid, and is therefore iodic anhydride, or the anhydride of iodic acid. It is decomposed when heated to $300^\circ C$., and is the most stable of any of the compounds of the halogens with oxygen.

96. Iodic Acid, HIO_3 .—Iodic acid is similar to chloric and bromic acids, but is more stable. It can be prepared by treating iodine with a strong oxidizing agent, as, for example, concentrated nitric acid. It can also be obtained by passing chlorine through water in which iodine is suspended, when iodic and hydrochloric acids are formed according to the equation:



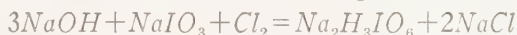
Iodic acid is a crystalline solid that decomposes into water and iodine pentoxide at $170^\circ C$., according to the equation:



97. Periodic Acid, HIO_4 .—The normal periodic acid has not been produced. The hydrate, $HIO_4 \cdot 2H_2O$, or H_5IO_6 , is formed by the action of iodine on perchloric acid:



It is a solid crystalline body that fuses at 130° C. and decomposes at a higher temperature. Its salts are formed by oxidizing or heating iodates. The simplest way to prepare a periodate is to lead chlorine into a solution containing sodium hydrate and sodium iodate, when the following reaction takes place:



The salt $Na_2H_3IO_6$ is evidently derived from the acid H_5IO_6 . From it the corresponding silver salt, $Ag_2H_3IO_6$, can be prepared; when this is treated with nitric acid it is converted into $AgIO_4$. The latter acid is normally given as periodic acid, and the compounds H_3IO_5 and H_5IO_6 , which contain 1 and 2 molecules of water, respectively, are called *hydrates*. The fact that salts derived from these acids are known, makes it appear probable that the oxygen and hydrogen are in the form of hydroxyl groups instead of in the form of water.

INORGANIC CHEMISTRY FOR PHARMACY STUDENTS

(PART 4)

SULPHUR, PHOSPHORUS, AND ARSENIC

INTRODUCTION

CRYSTALLOGRAPHY

1. Crystallization. — Although crystallography is not properly a part of chemistry, some knowledge of this subject is of such importance to the chemist that it will be briefly treated at this point.

Most chemical substances, when they pass from the liquid or gaseous into the solid state, assume some definite geometric form, or are said to *crystallize*. Crystals are produced when a substance, such as potassium nitrate, is dissolved in water and the solution is allowed to evaporate gradually; when a body, such as sulphur, is melted and allowed to solidify by cooling; or when a volatile substance, such as iodine, is vaporized, and the vapor condensed on a cool surface.

When a solution will dissolve no more of the solid, at a given temperature, the solution is *saturated*. If, however, the solution is boiled in a flask the solution will generally dissolve some more of the solid and become *supersaturated*. If a small crystal of the solid is dropped into a supersaturated solution, crystallization will immediately begin and will continue until the point of saturation is reached.

2. Crystal Structures.—Many native minerals exhibit perfect crystalline forms, though investigations have not yet disclosed the process of their formation. Judging from their perfect shape the assumption is justified that the process of their formation must have been a necessarily slow one. Besides their regular shape, these crystalline bodies possess other remarkable properties, that is, a peculiar power of splitting in certain directions more readily than in others, a property that is known as *cleavage*; and in many cases they possess the property of allowing light to pass more readily in certain directions than in others, giving rise to the well-known phenomena of *double refraction*.

A body assuming two distinct crystalline forms is said to be *dimorphous*; the study of even the more familiar elements includes some very important instances of dimorphism. A body that does not assume a crystalline form is termed *amorphous*. Certain complicated structures of the vegetable and animal world exhibit a structure that, although non-crystalline, is not devoid of a certain definite arrangement, and to which the name *organized*, or *cellular*, *structure* has been given. A substance, however, may have both a crystalline and an amorphous variety.

As a rule, every particular substance possesses a definite form, in which it will always crystallize, and by which it may be distinguished; when a crystal is formed from aqueous solution, for instance, the most minute particle possesses the same crystalline structure and perfect form as the largest crystals.

Certain substances exhibiting a similarity in their chemical constitution are found to crystallize in the same forms; these are said to be *isomorphous*.

3. System of Crystallization.—Many thousands of crystal forms are known, but they can all be referred to six classes or systems. When reference is made to certain crystals or crystalline forms the illustrations shown in Figs. 1 to 16 should be consulted.

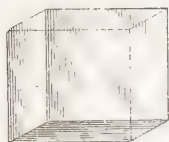
REGULAR, OR ISOMETRIC, SYSTEM

FIG. 1

Cube

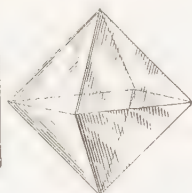


FIG. 2

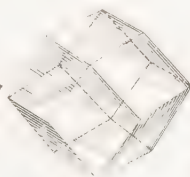
Regular
octahedron

FIG. 3

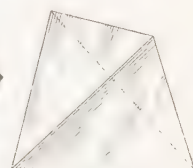
Rhombic
dodecahedron

FIG. 4

Regular
tetrahedron**QUADRATIC, OR TETRAGONAL, SYSTEM**

FIG. 5

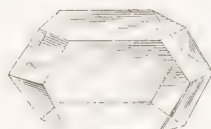
First right
square prism

FIG. 6

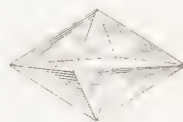
Second right
square prism

FIG. 7

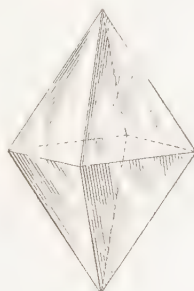
First right
square octahedron

FIG. 8

Second right
square octahedron

ORTHORHOMBIC, OR TRIMETRIC, SYSTEM

FIG. 9



FIG. 10

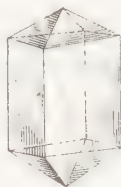


FIG. 11

Right octahedrons with
rhombic bases

Right rhombic prism

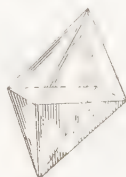
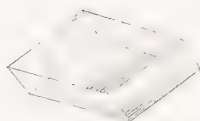
MONOCLINIC, OR MONOSYMMETRIC, SYSTEM

FIG. 12

Oblique rhombic octahedron

TRICLINIC, OR ASYMMETRIC, SYSTEM

Doubly oblique octahedron

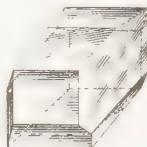


FIG. 13

Doubly oblique prism

HEXAGONAL SYSTEM



FIG. 14

Hexagonal prism



FIG. 15

Regular six-sided
pyramid

FIG. 16

Rhombohedron

SULPHUR

Symbol S. Atomic weight 32.06. Molecular weight 64.12. Valence II, IV, and VI.

1. Occurrence.—Sulphur, one of the earliest known elements, occurs free and in a combined state throughout nature in the neighborhood of active and extinct volcanoes. Its compounds occur in nature in much larger quantities, and more widely distributed, than the free sulphur itself. Combined alone with the metals it forms *sulphides* or *blendes*, and with metals and oxygen it forms *sulphates*. Compounds of sulphur are also found in the vegetable and animal kingdoms.

Sulphur forms an essential part of the animal tissues as a constituent of albumin, fibrin, etc., and it exists also, to a considerable extent, in the tissues of vegetables and plants; its compounds cause the peculiar odor of cruciferous and alliaceous plants, such as garlic, mustard, etc. It is found mostly in volcanic regions, those bordering on the Mediterranean being particularly rich in it. Formerly the chief source of sulphur was Sicily, but the United States is now entirely supplied by the sulphur mines or wells of Louisiana and Texas, and a large quantity is also sold for export. The annual consumption of this material, in this country, was, in 1919, about 673,000 tons.

Sulphur is also found in commercial quantities in Iceland, New Zealand, Japan, and Mexico.

The most important naturally-occurring compounds of sulphur are:

Sulphides: Iron pyrites, FeS_2 ; galena, PbS ; blende, ZnS ; cinnabar, HgS ; stibnite, Sb_2S_3 ; realgar, As_2S_2 ; orpiment, As_2S_3 ; copper pyrites, $CuFeS_2$.

Sulphates: *Gypsum*, $CaSO_4 \cdot 2H_2O$; heavy spar, $BaSO_4$; green vitriol, $FeSO_4 \cdot 7H_2O$; Glauber's salt, $Na_2SO_4 \cdot 10H_2O$; Epsom salts, $MgSO_4 \cdot 7H_2O$.

5. Preparation.—Commercial sulphur is the native material in a purified state; the native sulphur is commonly distributed in veins through masses of gypsum and celestine,



FIG 17

which must be separated from the sulphur by heat. This is accomplished by placing the native material in a row of earthen jars *A*, Fig. 17, heated by a long furnace, and provided with narrow tubes that convey the sulphur vapor into a second row of jars *B* that, standing outside of the furnace, act as receivers and condense the sulphur vapor into the liquid state, and from which it flows into vessels of water.

The sulphur thus obtained is exported as *rough sulphur*, and contains between 3 and 4 per cent. of earthy impurities, which must be removed by distillation. This redistilling, or refining process, is done in the apparatus shown in Fig. 18. A cast-iron cylinder *A* receives the melted sulphur from a tank *C* which is heated by the waste gases of the furnace. The sulphur vapor enters a large brick chamber *B*, the floor of which is slightly

inclined, so that the condensed liquid sulphur may flow toward a tap *H*, which can be opened when necessary. A damper *R*, which is regulated by a chain, permits the closing or opening of the cylinder *A*. The brick chamber *B* is provided with a safety valve *K*, which permits the escape of the expanded air.

At first, when the walls of the brick chamber are cold, the sulphur vapors condense in the form of a fine powder, known as *flowers of sulphur*; but when the walls of the chamber

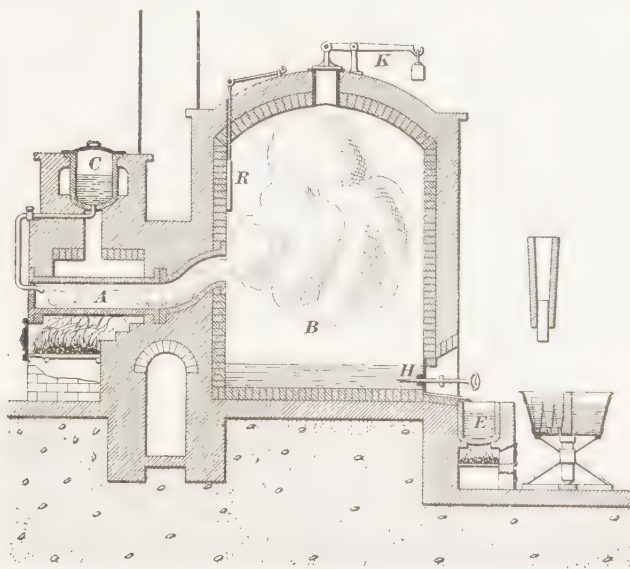


FIG. 18

become thoroughly heated, the sulphur vapors condense to a liquid, which, on the tap *H* being opened, is drawn into a vessel *E* and ladled into cylindrical molds, where it soon solidifies and forms the commercial product known as *brimstone*.

6. Frasch Process for Mining Sulphur.—In Louisiana, sulphur is mined by the Frasch process, which consists essentially of melting the sulphur, below the surface, by means of superheated water and then raising the molten sulphur to the surface by means of compressed air. The process may be described as follows:

A well 17 inches in diameter is bored to a depth of about 50 feet. Within this well a wrought-iron pipe, 13 inches in diameter, is sunk to a variable depth, sometimes as much as 250 feet. This pipe acts as a casing. Inside of the 13-inch pipe, an 8-inch pipe is sunk to the bottom of the sulphur bed, and in order to prevent plugging of the pipe at the bottom, that portion of it which is immersed in the sulphur is perforated, the holes being arranged in spiral form and about 6 inches apart. By means of this arrangement the hot water, led to the sulphur bed through this pipe, has access to the sulphur throughout the entire thickness of the deposit, and if the bottom of the pipe should become stopped, no trouble would be caused, by reason of the perforations at the bottom of the pipe. Inside the 8-inch pipe, a 6-inch pipe is sunk to the bottom of the sulphur bed, hot water being also pumped down this pipe. Inside the 6-inch pipe a 3-inch pipe is driven down to the sulphur bed and it is through this pipe that the molten sulphur reaches the surface. Finally, inside this 3-inch pipe, a 1-inch pipe is driven down to the sulphur, and it is through this pipe that the compressed air is forced.

7. Superheated water is pumped down the 8-inch and 6-inch pipes, the water from the 8-inch pipe melting the sulphur, which sinks down to the bottom of the sulphur bed. The hot water in the 6-inch pipe serves to keep the sulphur in the 3-inch pipe in a molten condition on its way to the surface. When sufficient sulphur has been melted (determined by practice), compressed air at a pressure of 250 pounds per square inch is forced down the 1-inch pipe and the liquid sulphur is pushed to the surface through the 3-inch pipe. Upon reaching the surface, the sulphur is conducted to roughly constructed bins, where it soon solidifies.

The sulphur produced by this method of mining has a purity ranging from 99.93 to 99.98 per cent. and contains very little water, if any. The Frasch process, however, can only be applied where the deposit is very rich in sulphur, and because of this reason, it has only been used with success in Louisiana and Texas and not in other parts of the world.

8. Physical Properties.—Sulphur exists in two distinct solid and liquid forms. Crystals of native sulphur, as well as those obtained by the evaporation of a solution, belong to the rhombic system of crystallization, illustrated in Figs. 9 and 19. Rhombic sulphur includes both roll sulphur and flowers of sulphur, and this variety is stable at temperatures below 96°C .; above this temperature it changes slowly over to *monoclinic sulphur*. Rhombic sulphur melts at 114.5°C .

9. When melted sulphur is allowed to cool slowly, long, prismatic, needle-like crystals are deposited, of the form shown in Fig. 20, which melt at 119.25°C . These crystals, which are known as **monoclinic sulphur**, are at first perfectly transparent, but after a short time become entirely opaque, through each breaking up into a number of minute rhombic crystals. Monoclinic sulphur can only be kept, as such, at a temperature above 96°C ., and below its melting point, 119.25°C .



FIG. 19

FIG. 20

10. If sulphur is dissolved in carbon disulphide and the liquid allowed to evaporate, the sulphur is obtained in crystals of the rhombic system. These are permanent in air, and the form is that in which the native sulphur crystals occur. If sulphur is heated above its melting point, and the application of heat is continued, a remarkable series of changes ensue. The color gradually darkens as the temperature rises; at the same time the liquid becomes thicker until, at a temperature near 160°C ., the mass is almost black and so viscous that the vessel may be inverted without the sulphur running out. With a further increase in temperature, beyond 260°C ., the sulphur again becomes liquid but remains of a much thicker consistency than it possessed when first melted. If, while in this state, it is poured into water, a soft, rubber-like, plastic sulphur of an allotropic variety, known as *soft sulphur*, is obtained. The difference between this variety and the common brittle form of sulphur is very striking. In about an hour, however, at 100°C ., it loses its tenacity and again becomes opaque and brittle. All varieties of sulphur boil at 444.6°C .

11. Chemical Properties.—Chemically, sulphur is an active element. When metals, with the exception of gold and platinum, in a very finely divided state are intimately mixed and rubbed together with powdered sulphur, a reaction takes place and the sulphides of the metals are produced. Thus,



Most metals when heated with sulphur combine energetically, the sulphides of the metals again being formed. Sulphur also unites with non-metals, such as chlorine and oxygen, to form chlorides and oxides, respectively. Sulphur is slowly oxidized to sulphuric acid by the oxygen of the air in conjunction with atmospheric moisture:



12. Uses of Sulphur.—Sulphur finds extensive employment in the arts and in various manufacturing and industrial processes, such as the manufacture of sulphuric acid, carbon bisulphide, gunpowder, and sulphur dioxide, in which form it serves as a bleaching agent. Sulphur and sulphur compounds are also used to a great extent in the paper and in the rubber industries. (U. S. P., pages 94, 330, 419, 420, and 482.)

HYDROGEN SULPHIDE

Formula H_2S . Molecular weight 34.076

13. History and Occurrence.—Hydrogen sulphide, also known as *sulphureted hydrogen*, was discovered by Scheele in the year 1777. It occurs in certain volcanic gases, and is the essential constituent of the water of the so-called sulphur springs, among the best known of which are Sharon and Avon, in the United States; Harrowgate, in England; Aix-la-Chapelle, in Germany; and Bagnières, in France. It is found in the gas of eggs and sewers, being produced by the decomposition of the albuminoids.

14. Preparation.—In the laboratory the gas is generated by the action of either dilute hydrochloric acid or dilute sulphuric acid on ferrous sulphide.

EXPERIMENT.—A small quantity of iron sulphide is placed in the bottle *A* of the apparatus shown in Fig. 21. Dilute acid, about 1 part acid to 3 parts of water, is added through the funnel tube of *A* until the bottle is about one-third full. The gas is then conducted through the flask *B*, containing water to wash the gas, into a bottle as shown, or into any other vessel of water, or any other liquid on which the gas is intended to act.

When desired to stop the evolution of gas the acid is poured off, leaving the iron sulphide at the bottom of the bottle. If desired, the

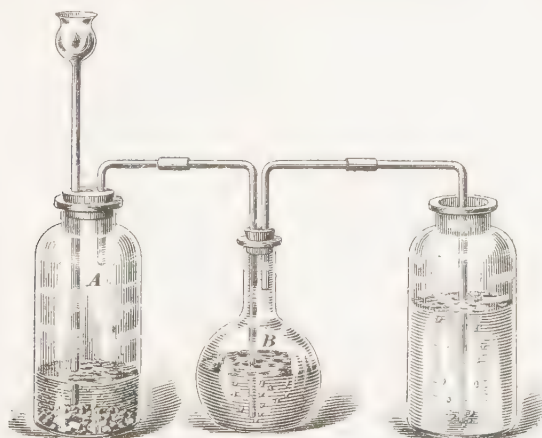
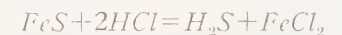


FIG. 21.

acid liquid can be set aside, when green crystals of ferrous sulphate, $FeSO_4 \cdot 7H_2O$, will form.

The following reactions take place in the preparation of hydrogen-sulphide gas, depending upon the kind of acid used:



15. For the continuous preparation of hydrogen sulphide from ferrous sulphide and dilute sulphuric or hydrochloric acid, in the larger laboratories, *Kipp's apparatus*, shown in Fig. 22, is very convenient. It consists of three glass bulbs, the two lower ones *A* and *B* being in a single piece, and the upper one *C* prolonged by a tube *D* reaching to the bottom of the lowest one, being ground air-tight into the neck of the second. Through the tubulure *E*, the ferrous sulphide, in fragments about the size of a chestnut, is introduced, the space

between the tube and the side of the constriction being too narrow to let them drop into the bulb *A*. This tubulure *E* is then closed by a stopper, through which a glass tube with a stop-cock *F* passes. The diluted acid (in the proportion of

1 part of acid to 9 parts of water) is poured through the opening *G* in the bulb *C*, and runs into the bulb *A*, and rises to overflow the iron sulphide in bulb *B*. If the stop-cock *F* is open, the evolved gas escapes; but when it is shut the pressure of the accumulating gas forces the liquid away from the sulphide down into the bulb *A*, and thence back into bulb *C*, thus stopping the action of further generating, and, at the same time, preserving a certain volume of hydrogen sulphide always ready when required. The acid, when saturated, is removed through the tubulure *H*.

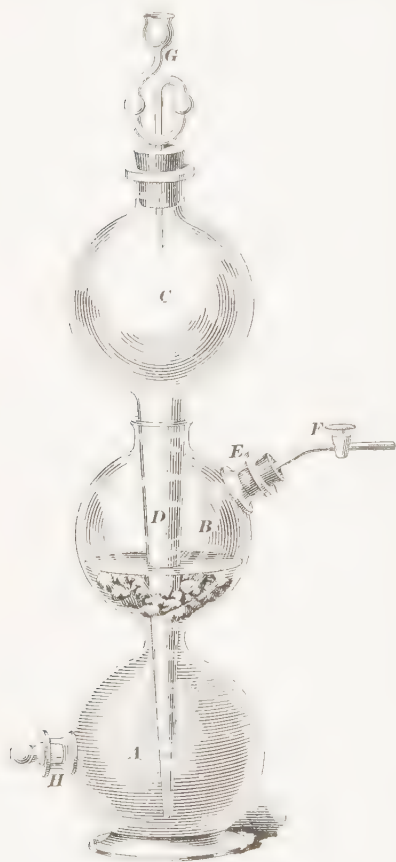


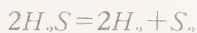
FIG. 22

16. Physical Properties.—Hydrogen sulphide is a colorless gas having the characteristic odor of rotten eggs. It is heavier than air, having a specific gravity of

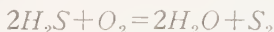
1.18 at 15° C. Cooled to − 74° C., or submitted to a pressure of 17 atmospheres at 10° C., it condenses to a colorless liquid having a specific gravity of .90. This liquid freezes to a solid at − 83.8° C., and boils at − 60.2° C. It is soluble in water, 1 part dissolving 4.37 parts of the gas at 0° C.; at 40° C., the

solubility of the gas is much less, 1 part of water dissolving only 1.86 parts of the gas, which may be completely expelled from a solution by boiling it. The gas is very poisonous, and when being used or generated in the laboratory, the work should be carried out under a hood, in order that any gas which escapes may pass out and not enter the room. If a hood is not available, however, the room should be well ventilated, but under no circumstances should one breathe air contaminated by this gas, for any length of time.

17. Chemical Properties.—In water solution, the gas shows the properties of a weak acid, turning blue litmus paper red, and for this reason it is also called hydrosulphuric acid. It is easily decomposed into hydrogen and sulphur at 400°C .



The gas reacts with metals and their oxides to produce sulphides, setting hydrogen free in the first case and water in the second. In the form of a gas or in solution, it is converted into water and sulphur by all oxidizing agents.



The affinity possessed by hydrogen sulphide for oxygen enables it to remove the latter from its compounds, thus acting as a reducing agent.

OXIDES AND ACIDS OF SULPHUR

18. Sulphur forms the following series of oxides and acids:

Sulphur dioxide, SO_2	Hyposulphurous acid, $\text{H}_2\text{S}_2\text{O}_4$
Sulphur trioxide, SO_3	Sulphurous acid, H_2SO_3
	Sulphuric acid, H_2SO_4

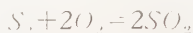
SULPHUR DIOXIDE

Formula SO_2 . Molecular weight 64.06

19. History and Occurrence.—Attention was first called to sulphur dioxide by the alchemist Stahl, but not until 1774 did Priestly carefully investigate this compound and its

properties. In nature, sulphur dioxide is but rarely met with; it exists, however, in the gases issuing from volcanoes. Although constantly discharged into the air of towns by the combustion of coal (which always contains more or less sulphur), it is so easily oxidized and converted into sulphuric acid that no considerable quantity is ever found in the atmosphere.

20. Preparation.—Sulphur dioxide is uniformly the product of the combustion of sulphur in air or in pure oxygen, being formed thus:



When needed for laboratory use it is generally prepared by heating sulphuric acid with metallic copper:



On a large scale it is prepared by heating carbon and sulphuric acid together. Carbon dioxide is also evolved, but this is not detrimental when the sulphur dioxide is used for the manufacture of sulphites. The equation governing this reaction is:



In the manufacture of sulphuric acid the main source of sulphur dioxide is the burning of iron pyrites.

21. Physical Properties.—Sulphur dioxide is a heavy, colorless gas, with a pungent, suffocating odor resembling that of a burning sulphur match. It is more than twice as heavy as air, its specific gravity being 2.23. Cooled to -10° C., it condenses to a thin, colorless liquid, with a specific gravity of 1.49; this liquid freezes at -76.1° C.

The gas is very soluble in water, one part of which dissolves 797.9 volumes at 0° C. and 156 volumes at 50° C. The solution may be completely freed from the gas by boiling.

22. Chemical Properties.—Sulphur dioxide is a stable gas, being decomposed only at high temperatures. The dry gas itself does not show an acid reaction with litmus, but its solution in water is decidedly acid.



The equation shows that sulphur dioxide is the *anhydride* of sulphurous acid. Sulphur dioxide is used as a refrigerating, disinfecting, and bleaching agent.

SULPHUR TRIOXIDE

Formula SO_3 . *Molecular weight* 80.06

23. Preparation.—Sulphur trioxide, or *sulphuric anhydride*, is prepared by passing a mixture of sulphur dioxide and oxygen over heated platinum sponge. Platinized asbestos may be used in place of the pure platinum sponge. The apparatus shown in Fig. 23 may be used to show the preparation of sulphur trioxide from sulphur dioxide. Oxygen is led through

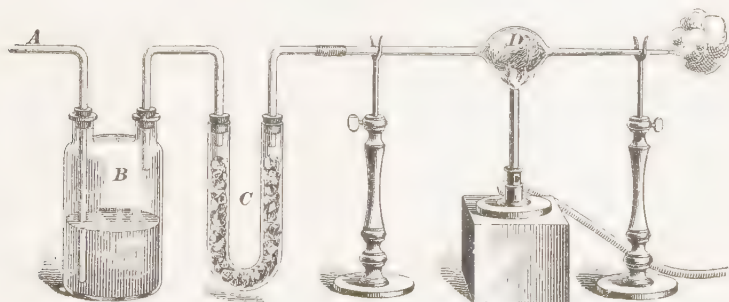


FIG. 23

the tube *A*, through a strong solution of sulphurous acid contained in *B*. Here the oxygen takes up sulphur dioxide and the mixture is passed through pumice stone in *C* soaked with sulphuric acid to remove all traces of moisture from the mixture, and then passed over the heated platinized asbestos in *D*.

24. Platinized asbestos may be obtained by wetting some asbestos with a solution of platinic chloride and heating this to redness, whereby the platinum is reduced to the metallic state, thus covering the asbestos with a thin film of platinum.

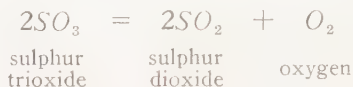
25. Physical Properties.—Sulphur trioxide exists in two distinct varieties or forms distinguished by the Greek names of the letters *a* and *b*, *alpha* and *beta*, or sometimes by the corresponding Greek letters, α and β . The alpha variety

is a colorless liquid with a specific gravity of 1.9229. It solidifies at 16.8° and boils at 44.88° . In contact with air, it fumes strongly, minute drops of sulphuric acid being formed.

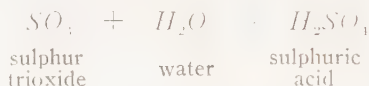


The beta variety probably has the formula $(SO_3)_2$; it exists in the form of silky needles, resembling asbestos. It has a specific gravity of 1.04 and melts at 50° C.

26. Chemical Properties.—On passing sulphur trioxide through a red-hot tube, it is separated into oxygen and sulphur dioxide.



Sulphur trioxide unites readily with water, with the evolution of great heat, producing sulphuric acid.



SULPHURIC ACID

Formula H_2SO_4 . Molecular weight 98.076

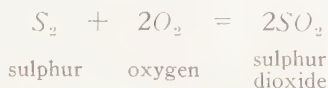
27. History.—The discovery of sulphuric acid dates back more than four centuries; it was first prepared by an alchemistically inclined monk, Basil Valentine, in the 15th century, who called it "*oleum sulphuris per campanum*." Doctor Roebuck, an Englishman, proposed the present method of manufacture in 1770. The acid thus prepared is therefore often called *English sulphuric acid*.

28. Importance of Sulphuric Acid.—There is no substance, with the single exception of water, that is so important to the chemist, be he manufacturing or analyzing, as sulphuric acid. The frequency of its application to various purposes in preceding experiments will give some idea of its usefulness and a familiarity with its properties, etc.

29. Preparation.—Sulphuric acid is manufactured on an immense scale in this country and in England, and is never

prepared in the laboratory for actual use, but always bought. A detailed description of the present process of manufacture will be very easily understood after a consideration of the principles of the chemical changes on which it depends.

Sulphur dioxide is produced by burning sulphur in the air, thus :



When sulphur dioxide is treated with an oxidizing agent in the presence of water it is converted into sulphuric acid, thus :



In practice the oxidation is principally accomplished by a mixture of nitric acid and nitrogen peroxide, NO and NO_2 , which acts like nitrogen trioxide, N_2O_3 , and is so written in the following equations. In starting the process, nitric acid is used as the oxidizing agent instead of nitrogen trioxide. The reaction is as follows :



After this the oxidation is accomplished principally by N_2O_3 , and the principal reactions are the formation of nitrosyl sulphuric acid, NO_2OHSO_2 , and the decomposition of this compound by water with the formation of sulphuric acid. These reactions are represented by the equations :



The nitrogen trioxide formed in the second reaction serves to oxidize a second portion of sulphur dioxide, so that theoretically a small quantity of this gas should be capable of oxidizing an indefinite quantity of sulphur dioxide, and in modern plants the waste of nitrogen trioxide is but slight.

The chemical principles illustrating the manufacture of sulphuric acid are shown in Fig. 24 and will aid in giving a clear understanding of the process employed in manufacturing sulphuric acid on a large scale.

A large Florence flask *A*, Fig. 24, is fitted with a stopper, through which pass several tubes: a tube *a* connected with a

flask *D* containing copper and strong sulphuric acid for evolving SO_2 ; a tube *b* connected with the flask *B* containing copper and dilute nitric acid for supplying nitrogen dioxide; a tube *c* connected with a small flask *E* containing water; a tube *f* for supplying air and preventing the pressure in *A* rising above that of the atmosphere. On heating the flask *B*, nitric oxide

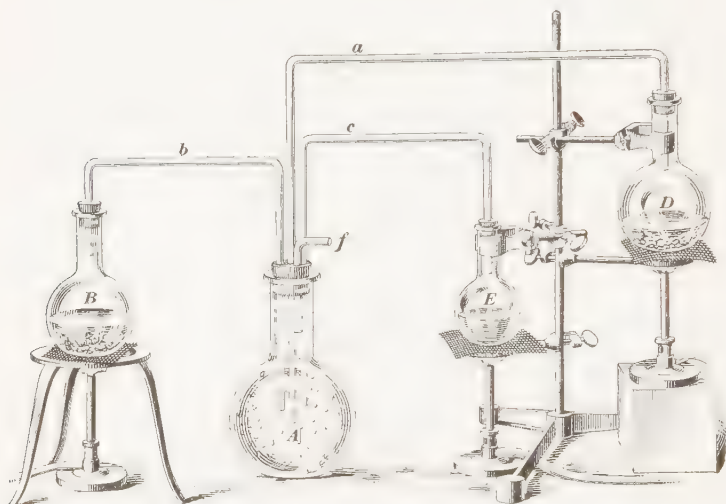


FIG. 1.

passes over into flask *A*, combines with the oxygen of the air and changes to nitrogen peroxide and nitric oxide. Flask *D* is then heated, when sulphur dioxide is evolved. This passes over into the flask *A* and decolorizes the red gas. The heat is then removed from the flask *D*, and steam is generated in flask *E* and sent into flask *A*, the nitrosyl sulphuric acid being decomposed and sulphuric acid formed.

COMMERCIAL MANUFACTURE OF SULPHURIC ACID

30. Lead-Chamber Process.—The manufacture of sulphuric acid on a commercial scale may be performed in the following manner:

Sulphur dioxide is produced by burning sulphur, or, more cheaply, by roasting sulphur ores, such as iron pyrites, FeS_2 , in

a suitable furnace, by which a mixture of air and sulphur dioxide is obtained. The reactions between the different substances then occur in large lead chambers made of timber framing and lined with sheet lead. Fig. 25 shows the general arrangement of a modern sulphuric-acid plant; *a, a* are two of a series of pyrite burners, generating sulphur dioxide, which, passing along the flue *b*, deposits dust containing oxides of iron and arsenic, and at the same time heats the cast-iron troughs *c, c*, which are supplied with sodium nitrate and sulphuric acid through the funnels *d* for the production of nitric-acid fumes, which together with SO_2 proceed onwards to the *Glover* tower *e*. This tower consists of a framework of timber supporting a

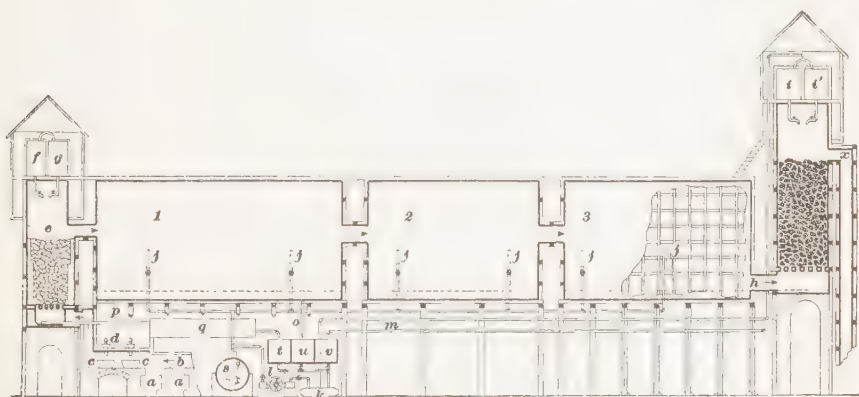


FIG. 25

column of thick sheet lead, and lined with a wall of refractory bricks built without mortar and diminishing in thickness toward the top. The remaining space is filled either with large flints or with reticulated, or "pigeon-holed," brickwork, through the interspaces of which the gases pass upwards, meeting on their way sulphuric acid trickling downwards from the tanks *f* and *g* on the tower top, and so reach the first leaden chamber *1*, which consists, as has been already explained, of a timber framework lined with lead and supported on cast-iron pillars. Into this chamber steam from the boiler *s* is introduced by the jets *j* set in the side of the chamber. Here the characteristic sulphuric-acid reaction occurs, and the acid collects on the bottom of the

chamber, which, for this purpose, has been shaped like a huge saucer.

31. In the first chamber 1, Fig. 25, most of the SO_2 is converted into H_2SO_4 , and the remaining gases, in which oxides of nitrogen begin to predominate, pass to a second chamber 2, where they again meet steam, and a further precipitation of sulphuric acid takes place, leaving the remaining gases still richer in nitrogen compounds and poorer in sulphur dioxide and acid to pass into the next chamber 3, where nearly the whole of the SO_2 is converted into liquid H_2SO_4 . The remaining gases, which, theoretically, should now only consist of residual nitrogen, a necessary excess of oxygen, oxides of nitrogen, and a trace of sulphur dioxide, pass from this chamber by the flue *h* to the *Gay-Lussac*, or *absorbing*, tower, which consists of a timber framework lined with lead, inside of which is built a wall of bricks without mortar. The inside space of this tower is filled with hard coke, down which sulphuric acid (specific gravity 1.75) trickles from the cisterns *i*, *i'*. This acid meets and absorbs the nitrogen oxides from the escaping gases, leaving only the excess of air, the atmospheric nitrogen corresponding to the oxygen taken up in the reactions, and a minute trace of SO_2 . These pass from the tower by the exit flue *x* to the chimney of the works, which produces the draft for the apparatus, their escape being regulated by a damper not shown in the figure. The number of chambers in a series varies from two to six in different works; their shape and size also vary within certain limits, the average size being 100 ft. \times 20 ft. \times 20 ft.

32. It now only remains to explain the workings of the towers, Fig. 25. Sulphuric acid of a specific gravity of 1.75 is run from the cistern *l* containing strong acid into a closed cast-iron vessel *k*, known as the *egg*. When the egg is filled, the valve communicating with the cistern is closed, and a valve is opened that connects the egg with a powerful air-pumping engine *l*, that, working at a pressure of 60 pounds per square inch, forces the acid out of the egg, up the pipe *m* into the cisterns *i*, *i'* at the top of the absorbing tower, whence it slowly

trickles down through the coke, taking up the nitrogen compounds, and running by way of the pipe below *m* to the cistern *v*, whence, as required, it is run into the egg and forced through a pipe similar to *m*, but not shown in the figure, to the cistern *f* on top of the Glover tower. The acid made in the chambers, and which possesses a specific gravity of 1.6, is drawn from time to time by pipe *o* into the so-called *chamber-acid cistern* *u*, from which it is blown into cistern *g* on the Glover tower. The run of nitrogen containing acid from cistern *f* and of chamber acid from cistern *g* is so adjusted that, after trickling down the hot flints or bricks and meeting the hot mixture of gases on its way through the tower, the acid runs off by the pipe *p*. Deprived of its nitrogen compounds, which enter the chambers, and concentrated by the heat to a specific gravity of from 1.73 to 1.75, it passes through a coil of lead piping immersed in cold water in the cooler *q*, which cools it from about 72° C. to about 16° C., thence to the strong-acid cistern *t*, whence it is taken for use as required.

33. It will be easily understood that the two towers effect an economy by considerably reducing the necessary amount of the most costly raw material, sodium nitrate, and that the Glover tower saves a considerable amount of coal by concentrating the acid and thus supplying steam to the chambers by utilizing the heat from the pyrite burners. Moreover, by cooling, and, consequently, contracting the volume of the gases, it makes the existing chamber capacity so much more effective. The acid is further concentrated by evaporation in either glass or platinum vessels until a specific gravity of about 1.83 is reached, when it is brought into commerce as *concentrated sulphuric acid*.

34. Contact Process.—A process that has been introduced successfully in the last few years is the *catalytic*, or *contact*, *process*. It depends on the fact that oxygen in the presence of platinized asbestos converts sulphur dioxide into sulphur trioxide; this with water gives sulphuric acid. The difficulties attending this process are very great; but they have been entirely overcome, and more than one factory is using this

process for the manufacture of both sulphuric acid and sulphur trioxide from air and sulphur dioxide, without the use of oxides of nitrogen.

In this process one of four contact masses may be used, namely, (1) asbestos, clay, pumice, or other porous material coated with platinum; (2) crusts formed of an earthy or alkaline water-soluble salt coated with platinum; (3) porous or fibrous materials such as in (1) coated with copper sulphate; (4) ferric oxide (roasted pyrites). The second mass has a great advantage over the others, due to its activity on account of the fine division of the platinum and the relatively small quantity of platinum required, 1 per cent. and less of platinum being very efficacious, both because of its fine division and because the base used also possesses catalytic activity. It can also be readily regenerated and the platinum can be easily and completely recovered.

35. In Fig. 26 is shown a diagram of the apparatus used in a sulphuric-acid plant

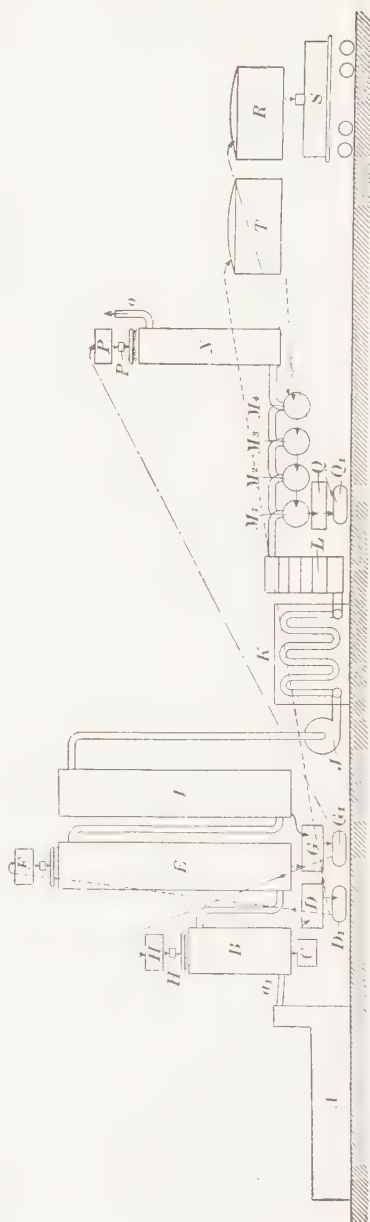


FIG. 26

employing the contact process. The course of the various materials and products is indicated by the arrows. *A* is a bench of pyrites burners. The burner gas passes through the flue a_1 to the first cleaning tower *B*. Weak sulphuric acid is constantly flowing down this tower, becoming concentrated by the hot burner gas and absorption of the sulphur trioxide contained in the burner gas, and finally flows out at the bottom into the cooler *C*. From the cooler *C*, the strong acid passes to the tank *D* and is delivered by the pump D_1 to the storage tank *T*, or to the tank *F* over the second cleaning tower *E*. A constant stream of strong sulphuric acid from the tank *F* is kept flowing down this tower. In this tower, the burner gas coming from the top of *B* is further cleaned and is then dried in the tower *I*; the circulation of the gases through the train of apparatus is maintained by the fan *J*. Before entering the contact ovens, the mixed gases are reheated to the proper temperature for the combination of the sulphur dioxide and oxygen in the reheater *K* and then are converted into trioxide in the contact oven *L*.

The sulphur trioxide now passes through the absorption cylinders M_1, M_2, M_3, M_4 . These are connected in such a way that the gas passes from end to end, meeting the weak acid flowing in the opposite direction. Both the gas and the acid in M_1 are richest in sulphur trioxide, while in M_4 the gas and acid are weak. The strong acid coming from M_1 is ready for the market; it is collected in the tank *Q*, and delivered to the storage tank *R* by the pump Q_1 . In order to recover the small amount of unabsorbed sulphur trioxide in the gases coming from M_4 these gases are passed through the tower *N*, which is supplied with weak acid from the tank *P*, which absorbs the last traces of the trioxide. The nitrogen and oxygen remaining pass into the air through the pipe *o*. From the tank *R* the acid is loaded into a tank car *S* for shipment.

PHYSICAL AND CHEMICAL PROPERTIES OF SULPHURIC ACID

36. Physical Properties.—Sulphuric acid, when pure and of 100 per cent. strength, is a dense, colorless acid of oily consistency, having a specific gravity of 1.83 at 18° C. When cooled it solidifies, the crystals formed melting at 10.46° C. Pure sulphuric acid may be distilled, but undergoes partial decomposition and loses more sulphur trioxide than water until an acid boiling at 338° C. and containing 98.3 per cent. of sulphuric acid is obtained.

Sulphuric acid possesses a very strong attraction for water, combining with the moisture of the air, and from its avidity to absorb water is largely used in the laboratory as a drying agent for gases, the gas to be dried being caused to bubble through it.

37. Chemical Properties.—Sulphuric acid attacks most organic substances, removing the water from them, and thus completely charring or blackening them. When bodies have an excess of carbon that element is liberated.

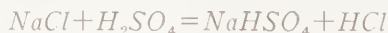
EXPERIMENT.—Prepare a saturated solution of sugar and water; pour about 5 cubic centimeters of it into a beaker, and add all at once 10 cubic centimeters of sulphuric acid; the mixture suddenly froths up with great heat, a blackened and charred mass remaining.

38. Salts of Sulphuric Acid.—Sulphuric acid, being dibasic, forms two well-marked series of salts; one normal, known as *normal sulphate*, but the other, still containing half of the hydrogen, is acid and is therefore called *acid bisulphate*. At a red heat the acid is decomposed into water, sulphur dioxide, and oxygen.

The normal sulphates, which are neutral, are made by allowing sulphuric acid to act on sodium chloride at high temperatures; thus:

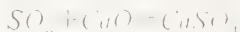


At lower temperatures the bisulphate is formed; thus:



Normal sulphates may also be made as follows:

1. Passing SO_3 over the oxide of a metal at red heat,



2. By precipitation,



3. By oxidation of sulphides,



39. Uses of Sulphuric Acid.—Concentrated sulphuric acid is used directly or indirectly in hundreds of industries. It is used in the manufacture of all other mineral acids and of many organic acids. Enormous quantities are used in the manufacture of fertilizers, alum, nitroglycerine and other explosives, in the refining of petroleum, and in the production of coal-tar dyes. Dilute sulphuric acid is used as the electrolyte in storage batteries and also in “pickling” or cleaning sheet iron before tinning or galvanizing. (U. S. P., pages 24, 25, 552, 575, 576, and 578.)

VARIATIONS OF SULPHURIC ACID

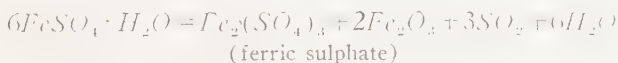
40. Pyrosulphuric Acid.—Pyrosulphuric, disulphuric, or Nordhausen sulphuric acid, $H_2S_2O_7$, is another kind of sulphuric acid met with in commerce. It may be regarded as a compound of a molecule of ordinary sulphuric acid with a molecule of sulphur trioxide:



It is prepared by the distillation of partly dried ferrous sulphate in earthen retorts; upon heating ferrous sulphate, $FeSO_4 \cdot 7H_2O$, 6 molecules of water of crystallization are expelled, leaving $FeSO_4 \cdot H_2O$, and when this salt is more strongly heated it breaks down into ferric oxide, Fe_2O_3 , sulphur trioxide, SO_3 , water, and sulphur dioxide, SO_2 ,



The above reaction, however, takes place in two stages, which are represented by the following equations:



The sulphur trioxide set free is absorbed in strong sulphuric acid,



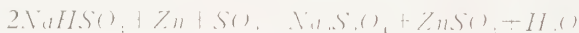
Pyrosulphuric acid is largely used in the production of coal-tar dyes and colors. It is a heavy, oily liquid of specific gravity 1.9. It is usually more or less dark colored, and hisses like a hot iron when dropped into water; it fumes strongly when exposed to air and is consequently very often called *fuming sulphuric acid*. It is now manufactured on a large scale by conducting *sulphur trioxide*, made by passing sulphur dioxide and oxygen over platinized asbestos at a high temperature, through ordinary sulphuric acid. It is sometimes called solid sulphuric acid, because it solidifies when cooled, forming crystals that melt at 35° C.

41. Hyposulphurous Acid.—Hyposulphurous acid, $H_2S_2O_4$, was first obtained by a German chemist named Schutzenberger by reducing sulphurous acid by means of zinc; thus,



As a result of the above reaction, a yellow solution results which possesses a strong bleaching power. The acid combines readily with oxygen and is a more active reducing agent than is sulphurous acid.

A salt of hyposulphurous acid may be prepared by the action of zinc on a solution of sodium acid sulphite, which contains an excess of sulphur dioxide,



42. Sulphurous Acid.—When sulphur dioxide is passed into water, part of it goes into solution and part combines with the water to form **sulphurous acid**, H_2SO_3 . This acid is very unstable and has never been isolated, its solution in water only being known. The acid being dibasic, forms two classes of salts, normal and acid, like Na_2SO_3 , *normal sodium sulphite*, and $NaHSO_3$, *acid sodium sulphite*.

Sulphurous acid is a good bleaching agent, it being extensively used for this purpose where delicate fabrics would be

destroyed by the stronger action of bleaching powder. (U. S. P., page 553.)

43. Thiosulphuric Acid.—Thiosulphuric acid, $H_2S_2O_3$, is only known in its water solution; but its salts, especially *sodium thiosulphate*, are in common use. Sodium thiosulphate is formed when a solution of sodium sulphite is boiled with sulphur; thus,



This salt is commonly, but erroneously, called *sodium hypsulphite*. It is used to a great extent in chemical analysis, in photography, and for the purpose of removing chlorine from fabrics which have been bleached. (U. S. P., pages 400, 550, 551, and 574.)

SULPHUR AND CHLORINE

44. Compounds of Sulphur and Chlorine.—Three compounds of sulphur and chlorine, (a) *sulphur monochloride*, S_2Cl_2 , (b) *sulphur dichloride*, SCl_2 , (c) *sulphur tetrachloride*, SCl_4 , are formed by the direct union of their constituents. The first is formed when the sulphur is present in excess, the last when the chlorine is most abundant.

(a) *Sulphur monochloride*, S_2Cl_2 , the most stable of the chlorides of sulphur, is an active, reddish-yellow liquid, specific gravity 1.709, possessing a peculiar, penetrating, disagreeable odor, fuming strongly in the air, and boiling at $138^\circ C$. It is decomposed by metals, liberating sulphur and forming the chloride of the metal. Sulphur readily dissolves in the monochloride, forming a thick liquid containing 66 per cent. of sulphur.

Sulphur monochloride is used extensively in the rubber industries, as a vulcanizing agent.

(b) *Sulphur dichloride*, SCl_2 , is prepared by passing chlorine to saturation into sulphur monochloride cooled by a mixture of ice and salt, and expelling the excess of chlorine by a stream of carbon dioxide. The compound thus obtained is a dark-red liquid boiling at $64^\circ C$., and having a specific gravity of 1.62. It decomposes even at ordinary temperatures into the monochloride and chlorine.

(c) *Sulphur tetrachloride*, SCl_4 , is prepared by saturating sulphur monochloride with chlorine at a temperature of -22°C . It is a yellowish-brown mobile liquid which only exists at temperatures below 0°C . When removed from a freezing mixture it immediately begins to dissociate with the evolution of chlorine.

SELENIUM

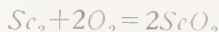
Symbol Se . *Atomic weight* 79.2. *Molecular weight* 158.4. *Valence* II, IV, and VI.

45. History.—The rare element selenium was discovered by Berzelius in the year 1817. The name, derived from the Greek word *moon*, was given the element because of its close chemical relation to the element *tellurium* (the earth). It is also closely related to sulphur in its physical characteristics and its chemical relations to other bodies.

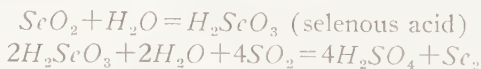
46. Preparation.—Selenium is prepared from the red deposit, found in the flue dust of sulphuric-acid works, by washing the scale with water and digesting with a *potassium cyanide solution* at 80°C . until the red color entirely disappears, *potassium selenocyanate*, KSeCN , being formed. The solution is then filtered and hydrochloric acid added to the filtrate, selenium being precipitated; thus:



This product is then purified by oxidation,



the oxide being sublimed and reduced to the metal by means of sulphur dioxide; thus,

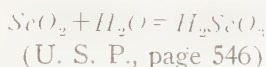


47. Compounds of Selenium.—Of the compounds of selenium, the following may be mentioned: (a) *Selenium dioxide*, and (b) *selenic acid*.

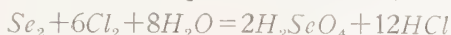
(a) **Selenium dioxide**, SeO_2 , is formed as follows:



It is readily soluble in boiling water, *selenous acid*, H_2SeO_3 , being formed,



(b) **Selenic acid**, H_2SeO_4 , is prepared by the action of chlorine on selenium in the presence of water,



Selenous acid and the selenites are converted into selenic acid and selenates in the same manner. By fusing selenium with potassium nitrate, the potassium salt of selenic acid is obtained,



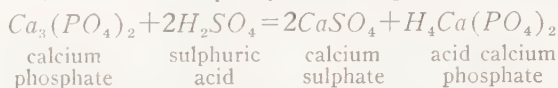
PHOSPHORUS

Symbol P. Atomic weight 31.04. Molecular weight 124.16. Molecule P₄. Valence III and V.

48. History and Occurrence.—Phosphorus was first obtained by Brand, of Hamburg, in 1669, by strongly heating a mixture of evaporated urine and white sand in an earthen retort. In 1771 Scheele found it could also be made from bones. Phosphorus derives its name from a Greek word meaning *light bearer*, from its property of giving light in the dark. Owing to its great affinity for oxygen, it is never found free in nature. It is, however, very widely distributed, and is found abundantly in the form of calcium phosphate, $Ca_3(PO_4)_2$. The minerals containing phosphates are subject to disintegration, and thus phosphorus is allowed to pass into the soil, from which it is extracted by plants. No plants will grow in a soil destitute of phosphorus, as it is required to build up certain parts of plant structure, particularly the fruit and seeds. As animals feed on plants, the phosphorus enters into their bodies, hence it occurs in the bones of animals, which contain about three-fifths of their weight of calcium phosphate.

49. Preparation.—Phosphorus is the only element for the ordinary preparation of which animal substances are

employed. It is prepared by treating burned bones with sulphuric acid, *acid calcium phosphate* being formed; thus,

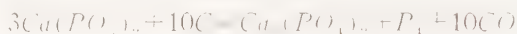


The mass is then digested in water, which dissolves the acid calcium phosphate, the resulting solution being then drawn off, evaporated, and the residue strongly heated with charcoal.

Upon evaporating the solution of acid calcium phosphate to dryness, this compound loses two molecules of water and is converted into calcium metaphosphate, $Ca(PO_3)_2$, thus:



and the calcium metaphosphate heated with charcoal forms phosphorus and calcium phosphate, $Ca_3(PO_4)_2$,



50. Commercial Manufacture of Phosphorus.—In the manufacture of phosphorus on a large scale the organic material in the bones is made use of in several ways. The bones are boiled with water, or treated with superheated steam, to extract the gelatin. Sometimes they are heated in iron retorts to distil off the ammonia and other volatile substances they contain. If the latter procedure is followed, the residue remaining after the distillation consists of bone black, bone coal, or animal charcoal, which is used in the manufacture of sugar, syrups, and various other articles. After the animal charcoal has become useless for these purposes it is completely burned in an open fire and thus converted into bone ash. To prepare phosphorus, the bone ash is mixed with two-thirds of its weight of strong sulphuric acid diluted with 18 to 20 parts of water, well stirred, and allowed to stand for about 12 to 14 hours. The clear liquid is strained off the sediment, which consists of calcium sulphate, evaporated in a pan to a syrupy consistence, mixed with one-fifth of its weight of charcoal, finely powdered, and heated to redness. The mixture is now distilled in bottle-shaped fireclay retorts 3 feet long. The arrangement of these retorts in the distilling furnace is shown in Fig. 27. As a rule, each furnace has 24 retorts placed in

two rows, one above the other. The temperature in the retorts *a* is raised to a bright red heat before they are charged with the mixture; the temperature is then increased to a white heat, which causes the phosphorus to distil over. The mouths of the retorts are connected to the pipes *b* which dip into troughs *c* containing water. These troughs run along the whole length of the furnace and in them the phosphorus condenses. The crude phosphorus is melted under hot water and thoroughly stirred, the greater proportion of the coarse suspended matter rising to the surface. Theoretically, the bone ash should yield

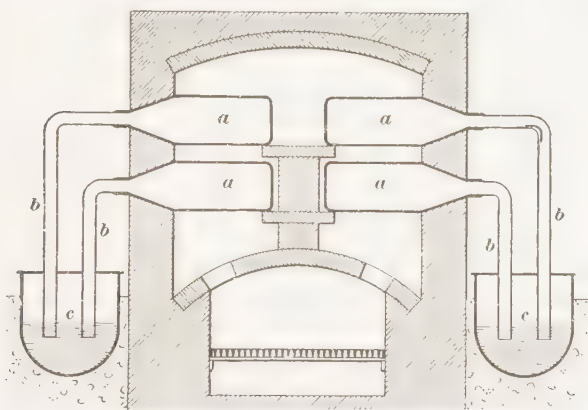


FIG. 27

about 11 per cent. of phosphorus, but practically hardly more than from 8 per cent. to 9 per cent. is obtained.

The crude phosphorus is purified by enclosing it in a chamois-skin sack, and strongly compressing it under water at 50° C.; the phosphorus passes through the leather and collects under the water. It is molded into sticks by being drawn into slightly conical glass tubes, which are then plunged into cold water. The phosphorus solidifies and is easily drawn from the tubes.

51. Phosphorus is prepared also by an electrical process known as the *Readman, Parker, and Robinson system*, in which the calcium phosphate is converted directly into phosphorus without previous treatment with sulphuric acid. The phosphate is mixed with charcoal and other fluxes, heated to as high

a temperature as possible, and then introduced into an electrical furnace. The electrical furnace used consists of an iron tank lined with refractory material, and contains large carbon electrodes in the sides. At the high temperature thus attained phosphorus vapor mixed with other gases passes over and is condensed. The slag formed is drawn off at intervals and fresh material charged into the furnace, thus making the process continuous.

52. Physical Properties and Varieties of Phosphorus.—Phosphorus is distinguished from all the other elements so far considered, in that it has 4 instead of 2 atoms in the molecule. This, however, does not mean that the molecule of phosphorus is twice the normal volume of other elements, which would be a contradiction of Avogadro's law, but simply that, with the same molecular volume as other bodies in the gaseous state, the phosphorus molecule contains 4 atoms.

53. Two varieties of phosphorus are known to exist, viz.: the *yellow* and the *red*. When first prepared away from light, **ordinary, or yellow, phosphorus** is an almost colorless, transparent solid having a specific gravity of 1.83. When exposed to light, however, its surface becomes coated with an opaque white film which soon changes to yellow, brown, and then red, and if exposed for a sufficiently long time the mass becomes red in color throughout.

At ordinary temperatures, 15° to 20° C., yellow phosphorus has the consistency of beeswax and may be easily cut with a knife. At the freezing point of water, however, it becomes rather brittle and shows, when broken, evidences of crystalline structure. It melts at 44.1° C. and boils at 290° C. It is slightly volatile at ordinary temperatures. When exposed to the air, which always contains some water vapor, white fumes are evolved which are poisonous and possess a garlic-like odor. In the dark, in contact with moist air, phosphorus emits a pale white light. Traces of naphtha or oil of turpentine destroy its luminous properties.

In match factories where large quantities of this variety of phosphorus are used, the workers frequently suffer from a

disease that attacks the teeth and jawbones and especially is this the case where the worker is exposed to phosphorus vapors.

Phosphorus is only slightly soluble in water, but dissolves readily in carbon disulphide, in phosphorus chloride, slightly in alcohol, and in ether, and in certain volatile oils. It is characterized by its great inflammability; at a temperature a little over its melting point it takes fire, and burns brightly with the formation of phosphorus pentoxide. Phosphorus is easily ignited by slight friction.

Owing to the readiness with which it undergoes oxidation, phosphorus is always kept under water, which liquid it does not decompose.

54. When yellow phosphorus is heated to a temperature of from 240° to 250° C. in a vessel from which air is excluded, **red phosphorus** is formed. This modification of the yellow variety exists as a dark-red powder, tasteless and non-poisonous, consisting of small flat crystals, having a specific gravity of 2.296. It has no odor, is not luminous when exposed to air, does not oxidize, and, consequently, need not be preserved under water. It remains solid up to a temperature beyond 250° C., and does not take fire when heated in the air until 260° C. is reached. At about this point it changes into the yellow variety and burns.

If the heating is conducted in a retort filled with carbon dioxide, so as to prevent combustion, the same weight of yellow phosphorus is produced, which proves most convincingly that the two varieties are only allotropic modifications of one and the same element. Further, both, on being burned, produce the same weight of phosphorus pentoxide, P_2O_5 .

The change from the yellow to the red variety is much accelerated by the presence of iodine in small quantities.

55. Chemical Properties of Yellow Phosphorus.

Phosphorus does not unite with pure dry oxygen at temperatures below 27° C., but, if the oxygen be slightly diluted with nitrogen, oxidation takes place. If traces of the vapors of ethylene, turpentine, or ether are introduced into the air surrounding glowing phosphorus, phosphorescence is immediately

destroyed. Chemically, yellow phosphorus is an active element; it unites vigorously with oxygen and the halogens and with sulphur and the metals at high temperatures.

56. Chemical Properties of Red Phosphorus. Chemically, red phosphorus is not as active as the yellow variety. Heated to 260° C. in air, it ignites, phosphorus pentoxide, P_2O_5 , being formed. Red phosphorus will burn if heated in an atmosphere of chlorine, but no heat is necessary

TABLE I
PROPERTIES OF YELLOW AND RED PHOSPHORUS

Properties	Yellow Phosphorus	Red Phosphorus
Color	Faint yellow	Red-violet
Smell	Garlic	Odorless
Exposure to air.....	Phosphorescence	No phosphorescence
Melting point	44.1° C.	725° C.
Physiological effects	Poisonous	Non-poisonous
Specific gravity	1.831	2.296
Solubility in carbon bisulphide	Soluble	Insoluble
Inflammability with chlorine	Ignites spontaneously	Ignites if heated

to cause yellow phosphorus to combine with chlorine. A summary of the properties of yellow and of red phosphorus will be found in Table I.

57. Uses of Phosphorus.—The greater part of the phosphorus produced is used in the manufacture of matches, but a small quantity is used in the manufacture of alloys, such as phosphor-bronze, in the manufacture of rat poisons, and in medicine. (U. S. P., page 319.)

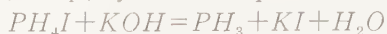
58. Matches.—The first matches were made about the year 1827. Up to this time fire had been artificially obtained by tinder and flint. The first matches were made of pieces of wood, the ends of which had been dipped into sulphur and coated with a mixture of sugar and potassium chlorate. These matches were ignited by being dipped into a bottle containing

collected in a jar, on standing, it loses this property of spontaneous inflammation, because the second phosphide, P_2H_4 , suffers decomposition. In this method of preparing the gas, milk of lime (that is, calcium hydroxide suspended in water) may be employed instead of potassium hydroxide.

Phosphine may also be prepared by treating *calcium phosphide* with water,



It is best obtained, however, by the decomposition of *phosphonium iodide*, PH_4I , by means of potassium hydroxide.



61. Properties of Phosphine.—Phosphine is a colorless gas with an unpleasant odor of putrid fish. It is sparingly soluble in water, is condensable to a liquid at -85° C., and is neutral in its reactions. It takes fire readily at 100° C., burning with a brilliant flame, but is not a supporter of combustion. The aqueous solution of phosphine decomposes in the light into hydrogen and red phosphorus. Phosphine is absorbed by solutions of copper sulphate and mercuric chloride, forming phosphides of the metals. It possesses, like ammonia, the property of combining with certain metallic chlorides, such as aluminum chloride, stannic chloride, and antimony chloride.

62. Phosphonium Compounds.—Phosphine acts like ammonia and combines with hydrobromic and hydriodic acids to form salts. In these salts, the group PH_4 acts like a metal and is termed **phosphonium**, just as the group NH_4 is called *ammonium*. The phosphonium compounds are not as stable as the ammonium compounds.

Phosphonium bromide, PH_4Br , is formed when hydrobromic acid and phosphine are brought together. The vapor has a specific gravity of 1.906. The bromide crystallizes in colorless cubes, and boils at 30° C.

Phosphonium iodide, PH_4I , is best prepared by adding yellow phosphorus to a saturated solution of hydriodic acid and after allowing this to stand for some hours, adding some iodine. It can also be prepared by decomposing phosphorus di-iodide with a small quantity of water. The iodide forms large, trans-

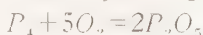
parent, glittering, quadratic prisms, fumes in the air, boils at 80° C., but it easily vaporizes at lower temperatures. It is easily decomposed with water. Phosphonium iodide is used as a powerful reducing agent and as the basis for the preparation of many organic phosphorus compounds.

OXIDES AND ACIDS OF PHOSPHORUS

63. The common oxides and acids of phosphorus are as follows:

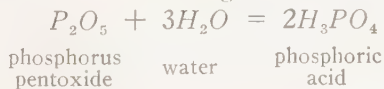
OXIDES	ACIDS
Phosphorus trioxide, P_2O_3	Hypophosphorous acid, H_3PO_2
Phosphorus pentoxide, P_2O_5	Phosphorous acid, H_3PO_3
	Metaphosphoric acid, HPO_3
	Orthophosphoric acid, H_3PO_4
	Pyrophosphoric acid, $H_4P_2O_7$

64. **Phosphorus pentoxide**, whose formula is P_2O_5 and whose molecular weight is 142.08, is always the product of the rapid combustion of phosphorus in the air or in oxygen. The reaction, which is synthetic, may be expressed by the equation:

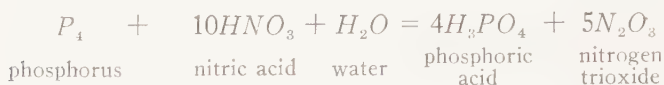


Phosphorus pentoxide is a snowlike, amorphous substance. It is fusible at red heat and is readily volatilized. When plunged into water it hisses, like a red-hot iron, but does not at once entirely dissolve, as a few flakes of metaphosphoric acid, HPO_3 , always remain suspended in the liquid for some time. Its great feature is its attraction for water; left exposed to the air for a few minutes only, it deliquesces entirely, becoming converted into phosphoric acid. It is often used in laboratories as a dehydrating agent, and will even remove water from oil of vitriol. It has no action on dry blue litmus paper.

65. **Phosphoric acid**, frequently called *orthophosphoric acid* to distinguish it from metaphosphoric, is obtained by the action of boiling water on phosphorus pentoxide. Its formula is H_3PO_4 , and its molecular weight is 98.06.



A method commonly employed for the preparation of phosphoric acid consists of oxidizing phosphorus with nitric acid, when the following reaction occurs :



This solution, on evaporation at the close of the reaction, yields a viscid liquid from which colorless crystals of phosphoric acid may be obtained.

Commercially, the acid, which, however, is somewhat impure, is prepared by treating bone ash (calcium phosphate) with sulphuric acid.

66. Phosphoric acid thus prepared is a syrupy liquid, which by evaporation gives hard, transparent, prismatic crystals that deliquesce in the air. The solution is intensely acid and is odorless. From ammoniacal solutions of magnesium sulphate, it precipitates magnesium ammonium phosphate—a white, crystalline compound—sometimes called *triple phosphate*. With silver nitrate, phosphoric acid, when neutralized by ammonia, gives yellow silver phosphate. On heating the aqueous solution of phosphoric acid to 213° C., pyrophosphoric acid is obtained, and on raising the temperature still higher, metaphosphoric acid. Phosphoric acid contains 3 atoms of replaceable hydrogen, and is consequently tribasic; it is therefore capable of forming acid, normal, and double salts. In the normal salts the 3 atoms of hydrogen is replaced by metals; but in the acid salts either 1 or 2 atoms of hydrogen may remain. The following series is illustrative of the various salts of phosphoric acid :

ACID SALTS

Primary sodium phosphate, H_2NaPO_4
 Secondary sodium phosphate, HNa_2PO_4
 Acid calcium phosphate, $HCaPO_4$

NORMAL SALTS

Potassium phosphate, K_3PO_4
 Barium phosphate, $Ba_3(PO_4)_2$
 Bismuth phosphate, $BiPO_4$

DOUBLE SALTS

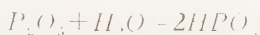
Ammonium magnesium phosphate, NH_4MgPO_4 Potassium barium phosphate, $KBaPO_4$

The acid and normal salts are called primary, secondary, or tertiary salts, according as 1, 2, or 3 hydrogen atoms are replaced to form them. (U. S. P., page 21.)

67. Metaphosphoric Acid.—In 1833, Graham showed that phosphoric acid loses water on being strongly heated, and that, on cooling, it becomes a transparent ice-like solid, which he named *glacial phosphoric acid*:



This acid is also prepared by dissolving phosphorus pentoxide in cold water:



Metaphosphates are produced by igniting primary phosphates:



or phosphates that have 2 molecules of volatile base:



hydrogen ammonium sodium phosphate	ammonium hydrate	sodium metaphosphate
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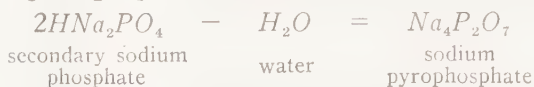
Metaphosphoric acid is obtained by decomposing metaphosphates. Its formula is HPO_3 , and its molecular weight is 80.048.

Metaphosphoric acid is a transparent, colorless, hard, glassy mass, that, though very soluble in water, is not crystallizable. Dissolved in water, it forms a strongly acid solution that gradually takes water from the air and forms orthophosphoric acid; this transformation is hastened by boiling. It possesses the property of coagulating albumin—a property that phosphoric acid does not possess—and gives a white precipitate with silver nitrate. Being monobasic, it forms but one class of salts. When the aqueous solutions of these salts are boiled they are converted into primary orthophosphates. It is distinguished by a remarkable tendency to produce polymeric forms, called di-, tri-, tetra-, and hexa-metaphosphates, respectively.

68. Pyrophosphoric, or Diphosphoric, Acid.—In 1826, Clark discovered a variety of phosphoric acid intermediate between the two forms described (produced by heating a solution of orthophosphoric acid to 240° C.); this he named pyrophosphoric acid. Two molecules of the orthophosphoric acid together lose 1 of water:



Pyrophosphates, sometimes known as *diphosphates*, are produced by igniting a phosphate that has 1 atom of hydrogen.



Pyrophosphoric acid generally occurs in solution, but may be obtained by evaporation at 213° C. as a soft glass or in semi-crystalline masses. Its solution is strongly acid, does not coagulate albumin, and gives a white precipitate with silver



FIG. 28

nitrate. Being tetrabasic, pyrophosphoric acid forms a large series of acid, normal, and double salts. Its formula is $H_4P_2O_7$.

On boiling its solution, pyrophosphoric acid takes up a molecule of water and becomes orthophosphoric acid; on igniting, it loses 1 molecule of water, becoming metaphosphoric acid.

69. Other Acids of Phosphorus.—Two other acids of pentad phosphorus are **phosphorous** and **hypophosphorous acids**. Phosphorous acid has the formula H_3PO_3 , is dibasic, and forms so-called phosphites. Hypophosphorous acid has the formula H_3PO_2 , is monobasic, and is obtained by decomposing barium hypophosphite with sulphuric acid. Hypophosphites are formed by boiling phosphorus in alkaline solutions.

70. Phosphorus trioxide, or phosphorous anhydride, P_2O_3 , is formed by heating phosphorus in a limited supply of air, as by putting a piece of phosphorus in a glass tube, such as shown in Fig. 28, drawing air through the tube,

and warming the tube gently. In this way not enough air can get access to the phosphorus to form the pentoxide. It is thus obtained as a waxlike mass. It may also be condensed in the form of feathery crystals. Phosphorus trioxide has an unpleasant garlic-like odor, melts at 22.5° C., and boils at 173° C. When pure it is unaltered by light, but when impure it changes to a dark-red color, due to the separation of red phosphorus. On exposure to the air the trioxide burns, forming the pentoxide. The trioxide is readily converted into phosphorous acid by water.

Other oxides of phosphorus have been prepared, but as they are of no importance and little is known of them, they will not be treated here.

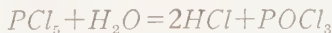
HALOGEN COMPOUNDS OF PHOSPHORUS

71. Phosphorus unites with the halogens to form compounds of the types PX_3 and PX_5 , X representing a halogen atom. The most important are the chlorides.

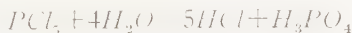
Phosphorus trichloride, PCl_3 , is a volatile liquid with a very pungent smell, formed by direct union of the elements. The product at first formed contains some pentachloride, which is removed by distilling with phosphorus. Water decomposes phosphorus trichloride, yielding hydrochloric acid and phosphorous acid:



By acting on phosphorus trichloride with chlorine, *phosphorus pentachloride*, PCl_5 , is formed. This is a solid that fumes strongly in moist air. By the addition of a little water it yields hydrochloric acid and *phosphorus oxychloride*, $POCl_3$;



with more water it yields hydrochloric acid and phosphoric acid:



ARSENIC

Symbol As. Atomic weight 74.96. Molecular weight 299.84. Molecular formula As₄. Valence III and V.

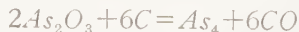
72. History and Occurrence.—While arsenic is a perfect analogue of phosphorus, it at the same time possesses a metallic luster and conducts electricity. It does not, however, form a base with oxygen. In its free state it is very similar to the metals. Sulphides and the oxides of arsenic have been known for many years. Brandt in 1773 was the first to carefully examine arsenic and to give it its place among the non-metals.

Arsenic occurs widely distributed both native and in combination with metals. Most sulphides of zinc and iron contain arsenic, hence it is very frequently found in these metals and in sulphuric acid made from the sulphide ores of these metals. Arsenic occurs most frequently as the sulphides, realgar, As₂S₂, and orpiment, As₂S₃, also as mispickel, FeS₂·FeAs₂, arsenical iron and nickel, FeAs₂, NiAs₂; smaltite, CoAs₂, and proustite, 3Ag₂S·As₂S₃. Arsenic is obtained in considerable quantities in the form of arsenious oxide as a by-product in the working of gold, silver, and lead ores.

73. Preparation and Properties.—Arsenic is obtained from arsenical pyrites, or mispickel, by heating it in earthen retorts; the arsenic, being volatile, sublimes and condenses in the cooler portions of the retort, toward its mouth. Thus,



In certain districts, arsenic is obtained by reducing its oxide with charcoal—a method by which it is obtained in a much purer form. Thus,



Arsenic presents the appearance of a dark, steel-gray, brittle solid, possessing a distinctly metallic luster, and having a specific gravity of 5.6 to 5.9. It occurs in two allotropic modifications, as, besides the steel-gray variety, which crystallizes in rhombohedrons, and possesses the above-mentioned specific

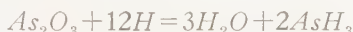
gravity, an amorphous, black, vitreous variety, of specific gravity 4.71, exists, which at 360° C. passes into the crystalline variety with considerable evolution of heat. Arsenic is volatile in closed vessels at 500° C.; its vapor is yellow and possesses a peculiar odor, which resembles that of garlic. In the air, it gradually oxidizes at ordinary temperatures, and at a red heat it burns with a bluish-white flame, producing arsenic trioxide. Arsenic and all its compounds are active poisons. (U. S. P., page 168.)

ARSENIC AND HYDROGEN

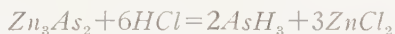
74. Arsine, or Hydrogen Arsenide.—The compound arsine, AsH_3 , is formed by the action of nascent, or atomic, hydrogen on solutions of arsenic compounds. Nascent hydrogen (written H) may be formed by the action of HCl or H_2SO_4 on zinc; thus,



When this hydrogen acts on solutions of arsenic compounds, arsine is formed; thus,



Arsine is also formed by the action of hydrochloric or sulphuric acid on zinc arsenide, thus:



Arsine is an extremely poisonous gas possessing a strong garlic-like odor, and great care must be taken when preparing it.

75. Marsh Test for Arsenic.—The importance of arsine lies in its application for the detection of arsenic in what is known as *Marsh's test*, which depends on the production of arsine whenever arsenic is in a solution in which nascent hydrogen is formed.

A convenient form of Marsh's apparatus is shown in Fig. 29. It consists of a three-necked Woulff's bottle *A*, through the middle tubulure of which a funnel *B* passes for the supply of liquid, while one of the side openings has a siphon tube *C* for withdrawing the exhausted acid, and the other tubulure has a delivery tube with a bulb *D*. This bulb is filled with cotton, to

retain any impurities that might be mechanically carried over by the gas. Attached to this leading tube is a jar *E* filled with potassium hydroxide and calcium chloride; the object of this mixture is to purify the evolved gas, which then passes through another leading tube *F*, made of hard glass and drawn out at intervals, as shown in the illustration.

Small pieces of pure zinc are first placed in the Woulff's bottle, to which is added pure sulphuric acid, previously diluted with 3 parts of distilled water and thoroughly cooled (so as to have normal temperature). After allowing sufficient time for the air to be expelled from the apparatus, the leading tube *F* is heated to dull redness by a Bunsen burner. If no dark

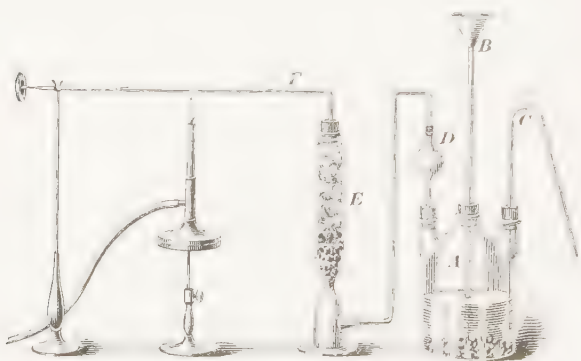


FIG. 29

deposit appears beyond the flame in 15 minutes, the materials employed may be considered free from arsenic. The liquid suspected to contain arsenic is then added through the funnel tube. If arsenic should be present, the flame of hydrogen burning at the end of the tube will, often in a few seconds, change its color, becoming whitish, and will deposit a dark-brown metallic spot on a porcelain plate held in the flame. If the tube is again heated, the arsine will be decomposed, and the arsenic be deposited as a dark metallic ring. According to Wormley, $\frac{1}{50000}$ grain of arsenic trioxide in 100 grains of the solution may be detected by this test.

When hydrogen is evolved from any liquid containing arsenic, traces of arsine are always formed; it can be detected

by the smell or by the previously mentioned tests, which are so delicate that .001 milligram of arsenic can be detected. By limiting the size of the apparatus and by observing all possible precautions .0005 milligram of arsenic trioxide, As_2O_3 , may be detected. (U. S. P., pages 553 and 584.)

OXIDES AND ACIDS OF ARSENIC

76. The oxides of arsenic, with their corresponding acids, are:

OXIDES	ACIDS
Arsenic trioxide, As_2O_3	Arsenious acid, H_3AsO_3
Arsenic pentoxide, As_2O_5	Arsenic acid, H_3AsO_4

77. **Arsenic trioxide**, As_2O_3 , or *arsenious anhydride*, has long been known under the names of *white arsenic* and *arsenious acid*. It is prepared by the roasting of ores containing arsenic, the vapors given off being condensed in long brick chambers, where they condense in the form of a white powder. It is purified by again subliming and recondensing.

78. Arsenic trioxide, sometimes called *arsenious oxide*, occurs in two distinct modifications. When the arsenic-trioxide vapor is condensed at a temperature of $400^\circ C.$, it forms the *first variety*, a transparent vitreous mass of a specific gravity of 3.738, which, when deposited slowly at a slightly lower temperature, crystallizes in right rhombic prisms. The *second variety* is obtained either by condensing the vapor at $200^\circ C.$, or by cooling a saturated aqueous solution of arsenic trioxide of the first modification, as brilliant transparent octahedral crystals of specific gravity 3.689. The vitreous modification passes gradually at ordinary temperatures, rapidly at about $100^\circ C.$, into the second variety, forming a white, opaque mass resembling porcelain, commonly known as *white arsenic*.

When the vitreous modification is dissolved to saturation in hot hydrochloric acid and left to cool slowly, it crystallizes in octahedrons, the formation of each crystal being accompanied by a flash of light.

Arsenic trioxide is frequently mistaken for flour, but it may be easily recognized by its weight and by sprinkling it on red-hot coal, when a strong odor of garlic is obtained.

Arsenic trioxide is only slightly soluble in water. The solution has a sweet, unpleasant metallic taste, is feebly acid, and is very poisonous. The best antidote for arsenic in any form is freshly precipitated ferric hydroxide. Workers in arsenic plants usually apply an ointment of ferric hydroxide and lanoline to their faces previous to beginning work. The ferric hydroxide is best precipitated by means of magnesium hydroxide. Ferric hydroxide forms an insoluble arsenite with the arsenic and thus prevents further absorption of the poison. The reaction of ferric hydroxide and arsenic is represented by the following equation:



(U. S. P., pages 64, 65, and 525)

79. Arsenious acid, H_3AsO_3 , is obtained when arsenic trioxide is dissolved in water. It has never been prepared in a pure state, as the solution probably is really a solution of the trioxide. This solution has a slight acid reaction and forms salts (*arsenites*). By exactly neutralizing the solution with ammonia and adding silver nitrate, a salt is obtained corresponding to the formula Ag_3AsO_3 , which shows the acid to be tribasic.

Several series of arsenites are known, namely, ortho-arsenites, meta-arsenites, and pyro-arsenites.

The alkali arsenites are soluble in water, absorb oxygen from the air, showing they are powerful reducing agents, they themselves being converted into arsenates. The alkali arsenites are frequently used in sheep dips and in sprays, and a soap containing these salts together with other ingredients is sometimes used to preserve the skins of animals.

80. Scheele's Green, or Copper Arsenite.—Scheele's green, $CuHAsO_3$, is formed when arsenious acid is dissolved in a solution of potassium carbonate and a solution of copper sulphate is added. Thus,



It is a very poisonous pigment sometimes used in the manufacture of wallpaper.

81. Reinch's Test for Arsenic in Wallpaper.—The sample of paper is soaked for some time in ammonium hydroxide, which dissolves copper arsenite. The solution is then acidified with hydrochloric acid, which should compose at least one-tenth of the volume of the solution, and boiling with a strip of bright copper, the arsenic is deposited on the copper as a gray film. To further identify the deposit, wash the copper with distilled water, dry, and heat in a glass tube, to obtain the arsenic mirror or the crystalline structure. All the reagents used must be tested for arsenic in the same manner to be perfectly sure that the arsenic is in the wallpaper.

82. Paris Green and Fowler's Solution.—Other well-known arsenites are *Paris green*, or *Schweinfurt green*, which is a copper aceto-arsenite made by mixing equal parts of hot solutions of arsenic trioxide and copper acetate, and *Fowler's solution*, which is prepared by dissolving arsenious acid in a solution containing an equal weight of potassium bicarbonate.

83. Arsenic pentoxide, As_2O_5 , is obtained as a white porous mass when arsenic trioxide is heated in the presence of an oxidizing agent to a temperature slightly below a red heat. Although arsenic resembles phosphorus very closely, it differs from the latter in that when burned in air or oxygen it oxidizes to the trioxide only. Arsenic pentoxide can be prepared directly from arsenic acid by heating it to a dull redness. Arsenic pentoxide has a specific gravity varying from 3.99 to 4.25, is slowly soluble in water, and deliquesces in moist air, forming arsenic acid. Heated to a bright red heat it decomposes into oxygen and arsenic trioxide, and heated with reducing agents it is easily reduced to free arsenic.

84. Arsenic acid, H_3AsO_4 , was first prepared by Scheele in 1775 by the oxidation of arsenic trioxide with nitric acid. He also prepared it by the action of moist chlorine gas on the trioxide; thus:



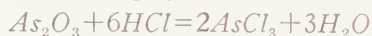
On evaporation, long rhomboidal crystals containing a small quantity of water of crystallization separate. These crystals deliquesce in the air, and when heated to 100°C. , lose their water of crystallization and yield ortho-arsenic acid, H_3AsO_4 . This acid possesses a very acid, unpleasant metallic taste, and is almost as poisonous as the trioxide. On heating the ortho-arsenic acid to 180°C. it loses water, and hard, glittering crystals of pyro-arsenic acid, $\text{H}_4\text{As}_2\text{O}_7$, are obtained. Between 200°C. and 204°C. , another molecule of water is expelled and a white crystalline mass of meta-arsenic acid, HAsO_3 , is left. On the addition of water, the last two acids are reconverted into ortho-arsenic acid.

Ortho-arsenic acid is readily soluble in water, is tribasic, and forms salts, the *arsenates*, isomorphous with the phosphates.

ARSENIC AND CHLORINE

85. The compounds of arsenic with the halogens are analogous with the corresponding phosphorus compounds. They are the result of the direct union of their constituents. The slight metallic character of arsenic is shown in the chloride which may be formed by the action of hydrochloric acid on the oxide.

86. **Arsenic trichloride**, AsCl_3 , is prepared by distilling arsenic trioxide with strong hydrochloric acid:



It can be prepared also by passing dry chlorine over heated white arsenic contained in a retort. The trichloride is then distilled over into a flask leaving a transparent glassy mass behind.

Arsenic trichloride is a colorless, oily liquid with a specific gravity of 2.21. It boils at 130°C. , evolving a heavy, colorless vapor, and solidifies in long, pearly needles at -18°C. It evaporates in the air, giving off dense white fumes, and is extremely poisonous. A small quantity of water dissolves arsenic trichloride without change, but considerable water decomposes it into hydrochloric acid and arsenic trioxide, thus:



87. Arsenic tribromide, $AsBr_3$, and **arsenic tri-iodide**, AsI_3 , are prepared in the same manner as the trichloride. The tribromide forms colorless, deliquescent crystals that melt at 31°C . and boil at 220°C . It has a strong odor of arsenic, and is acted on by water in the same way as the trichloride. Arsenic tri-iodide forms bright-red, hexagonal crystals, of a specific gravity of 4.4, and that melt at 140.7°C . (U. S. P., page 63.)

88. Arsenic forms two fluorides, the **trifluoride**, AsF_3 , and the **pentafluoride**, AsF_5 . The former is prepared by distilling arsenic trioxide with fluorspar and sulphuric acid. It is a transparent, colorless liquid that fumes strongly in the air; it has a powerful, pungent odor, solidifies at -8.5°C ., boils at 63°C ., and is decomposed by water. The pentafluoride is formed by distilling a mixture of arsenic trifluoride, antimony pentafluoride, and bromine. It is a colorless gas that liquefies at -53°C . and becomes solid at -80°C .

ARSENIC AND SULPHUR

89. Six sulphides of arsenic are known: Three arsenic subsulphides, As_3S , As_4S , and As_4S_3 ; arsenic disulphide, or realgar, As_2S_2 ; arsenic trisulphide, or orpiment, As_2S_3 ; and arsenic pentasulphide, As_2S_5 .

90. Realgar, or **arsenic disulphide**, As_2S_2 , occurs in nature in the form of transparent red crystals that belong to the type of the oblique rhombic prism. It is formed artificially by heating arsenic acid with the proper proportion of sulphur. It is fusible and may be crystallized by slow cooling. When strongly heated in a closed vessel, it boils and distils without alteration; but, when heated in the air, it burns into arsenic trioxide and sulphur dioxide. The alkaline sulphides and ammonium sulphide dissolve realgar, leaving a brown powder that is considered a subsulphide of arsenic. A boiling solution of potassium hydrate also dissolves realgar, forming a mixture of potassium arsenite and sulpharsenite; the latter is a soluble compound of arsenic trisulphide and potassium sulphide.

91. Arsenic trisulphide, or orpiment, As_2S_3 , is found in nature in yellow prismatic crystals. It may be obtained by fusing together arsenic and sulphur in the proper proportion, or arsenic trioxide and sulphur; in the latter case, sulphur dioxide is disengaged and arsenic trisulphide sublimes. Thus prepared, orpiment occurs as crystalline masses of a yellow, or, more correctly, yellow-orange color, and is of a pearly aspect. It is fusible and volatile, burning with a pale-blue flame.

92. Arsenic pentasulphide, As_2S_5 , is precipitated when an excess of hydrogen sulphide is passed into a solution of arsenic acid heated to 70° C. It is a lemon-yellow powder that is insoluble in water and may be fused and distilled without alteration.

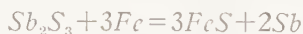
ANTIMONY, BISMUTH, AND SILICON

ANTIMONY

Symbol Sb. Atomic weight 120.2. Molecular formula Sb_2 . Molecular weight 240.4. Valence III and V.

93. History and Occurrence.—Antimony has been known for many hundred years; it was prepared in the pure state by Basil Valentine toward the end of the 15th century. It occurs in nature both free and in combination. Its most abundant source is the sulphide known as *stibnite*, found in China, Japan, Australia, the East Indies, and Hungary. It also exists in combination with oxygen in the minerals *valentinite*, *senarmontite*, and *cervantite*, with silver in *dycrasite*; and with silver and sulphur in *pyrargyrite* and *miargyrite*.

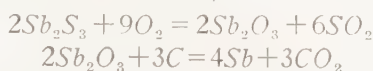
94. Preparation and Properties.—Antimony is obtained from its sulphide, Sb_2S_3 , by heating it in covered pots with metallic iron:



The excess of iron is removed by heating with charcoal and fluxes, such as sodium carbonate, and a further addition of the sulphide. The metal extracted in this way is contaminated with arsenic, iron, sulphur, and often lead or copper. It may

be further purified by remelting with potassium hydroxide when, on solidifying, it shows fernlike markings due to crystallization, and is known as *star metal*.

It is prepared also by roasting the sulphide, when the sulphur burns and antimony trioxide is formed. The oxide is then reduced with carbon. Thus,



Antimony is a brilliant, bluish-white, brittle element, of specific gravity 6.715. It crystallizes in rhombohedrons, thus being isomorphous with arsenic and red phosphorus. It melts at 630° C., and at a white heat may be distilled. It scarcely tarnishes in the air, but takes fire at a red heat, producing antimony trioxide. It is strongly attacked by chlorine, forming antimony trichloride, $SbCl_3$, and pentachloride, $SbCl_5$. Antimony is so brittle that its only use in the free state is for the construction of thermoelectric piles. It is used in several useful alloys, however, as, for example, in type metal, Britannia metal, pewter, in pharmacy, and in calico dyeing and printing. (U. S. P., page 50.)

ANTIMONY AND HYDROGEN

95. Stibine.—Antimony and hydrogen form a compound known as **stibine**, SbH_3 , which is similar to the hydrogen compounds of nitrogen, phosphorus, and arsenic in constitution, but it resembles arsine very closely. Stibine is a colorless, peculiarly disagreeable smelling, poisonous gas. It can be condensed to a colorless liquid that boils at -18° C. and solidifies at about -91.5° C. It is slightly soluble in water, and is very easily ignited, burning with a greenish-white flame and giving off white fumes of the trioxide.

Whenever an antimony compound is present in a solution from which hydrogen is being evolved (see Marsh test for arsenic) a gas escapes, mixed with the hydrogen, causing it to burn with a bluish-white flame. This gas is stibine, which is decomposed by heat, like arsine, but the metallic deposit of antimony is easily distinguished from that of arsenic by being

less volatile, by its darker color, its smoky appearance, its insolubility in hypochlorites, and its solubility in ammonium sulphide.

OXIDES AND ACIDS OF ANTIMONY

96. The three oxides and three acids of antimony known are:

OXIDES	ACIDS
Antimony trioxide, Sb_2O_3	Orthoantimonic acid, H_3SbO_4
Antimony tetroxide, Sb_2O_4	Metantimonic acid, $HSbO_3$
Antimony pentoxide, Sb_2O_5	Pyroantimonic acid, $H_4Sb_2O_7$

97. Antimony trioxide, Sb_2O_3 , occurs in nature as valentinite, or white ore of antimony. It is the product of the combustion of antimony in air or of its oxidation by nitric acid. The trioxide formed by burning antimony in air always contains some tetroxide, and by heating it long enough, at a sufficiently high temperature, it is completely converted into the tetroxide. Toward some of the stronger bases, like sodium hydrate, the trioxide acts as an acidic oxide. Toward most bases, however, it does not show acid properties, and toward the stronger acids it acts as a base. Oxidizing agents convert it into antimonic acid.

98. Antimony tetroxide, Sb_2O_4 , as previously stated, may be prepared by igniting the trioxide in the air. It occurs native as antimony ochre. It can be obtained more readily by igniting antimonic acid, H_3SbO_4 , thus driving off water and oxygen. At ordinary temperatures the tetroxide is white, but becomes yellow when heated. It has the properties of an acidic oxide toward strong bases, but toward strong acids it acts as a weak base.

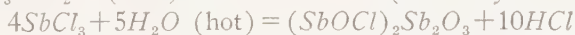
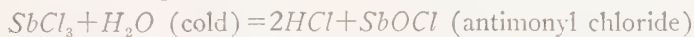
99. Antimony pentoxide, Sb_2O_5 , is prepared by gently igniting antimonic acid to expel water, but care must be taken not to heat it high enough to expel oxygen. It cannot be formed by the addition of oxygen to the tetroxide, but if ignited, easily breaks up into the tetroxide and oxygen.

100. Acids of Antimony.—Antimonic acid, H_3SbO_4 , is the final oxidation product when antimony is treated with

aqua regia. It may also be obtained by treating one of its salts with sulphuric acid. It is similar to phosphoric and arsenic acids and occurs in three forms. The ortho acid, H_3SbO_4 , is formed when antimony pentachloride is decomposed with water. When dried at 100°C ., the pyro acid, $H_4Sb_2O_7$, is formed, and when heated to 200°C . the meta acid, $HSbO_3$, results. The ortho and meta acids are white amorphous bodies soluble in potassium hydrate and only slightly soluble in water. The pyro acid, while only sparingly soluble in water is more soluble than is the meta; the normal fixed alkali salts of the pyro acid are soluble in water, and when heated to 200°C . the pyro acid is converted in the meta acid.

ANTIMONY AND CHLORINE

101. Antimony trichloride, $SbCl_3$, may be prepared by treating antimony directly with chlorine, or by dissolving antimony in hydrochloric acid with the addition of nitric acid and distilling the product. This compound is a solid crystalline substance that is quite soft, and on account of its consistency is called *butter of antimony*. It melts at 73°C ., boils at 223°C ., and deliquesces in the air. When treated with water an oxychloride is formed, the composition of which depends more or less on the temperature of the water. Thus,



If free hydrochloric or tartaric acids are present, precipitation is prevented.

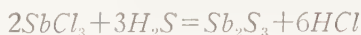
102. Antimony pentachloride, $SbCl_5$, may be obtained by treating the trichloride with an excess of chlorine. It is similar to phosphorus pentachloride, but is more readily converted into the trichloride according to the equation:



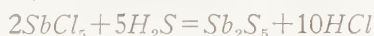
This is similar to the action of the pentoxide of phosphorus in breaking down into the trioxide and oxygen. When the pentachloride is acted on by water it at first yields an oxychloride, but by further action it yields antimonious acid, H_3SbO_4 .

ANTIMONY AND SULPHUR

103. Antimony trisulphide, Sb_2S_3 , occurs in nature as the mineral *stibnite*, and is the chief ore of antimony. It may be prepared by treating a solution of antimony trichloride with hydrogen sulphide, when the trisulphide separates as an orange-colored precipitate. The naturally occurring trisulphide is either gray or black. The reaction is as follows:



104. Antimony pentasulphide, Sb_2S_5 , may be prepared by passing hydrogen-sulphide gas into a solution of antimony chloride, acidified with HCl . Thus,



When dry it is a golden-yellow powder that readily dissolves in solutions of metallic sulphides, forming sulphantimonates.

BISMUTH

Symbol Bi. Atomic weight 208. Molecular formula Bi_2 . Molecular weight 416. Valence III and V.

105. History and Occurrence.—Bismuth was first distinctly recognized by Basil Valentine in the 15th century. Agricola, in 1529, called it *bismetum*, and Paracelsus mentions it as *wismeat*. It was for a long time confounded with other elements, especially with lead, tin, and antimony. Pott, in 1739, first described its characteristic actions. This element occurs in the native condition in veins traversing gneiss, clay slate, and other crystalline rocks. It also occurs as oxide, forming the mineral *bismite*; as sulphide, or *bismuthinite*; as sulphotelluride, or *tetradymite*; and as carbonate, or *bismutite*.

106. Preparation and Properties.—Bismuth for use in the arts is obtained on a large scale from the native bismuth by placing this, mixed with the rocky gangue, in iron tubes slightly inclined, which are heated in a furnace. The bismuth

melts and flows out at the lower ends of the tubes into suitable vessels, from which it is ladled into molds. The bismuth of commerce is mostly contaminated with arsenic, iron, and various other metals, from which it may be freed by fusion with potassium nitrate. Chemically pure bismuth may be obtained by reducing bismuth nitrate, $Bi(NO_3)_3$, with charcoal.

Bismuth is a hard, brittle, brilliant metal of a reddish-white color. It has a great tendency to crystallize on fusion; by melting a considerable quantity of it, allowing it to cool until a crust forms on the surface, piercing this and pouring out the portion that still remains liquid, crystals of great size and beauty may be obtained. Owing to a slight superficial oxidation, these crystals, as usually obtained, are beautifully iridescent. Bismuth has a specific gravity of 9.747; it melts at 368° C., and expands one thirty-second of its bulk in solidifying. It may be distilled at a white heat. It is unaltered in dry air, but is tarnished in the presence of moisture. Strongly heated, it takes fire, burning with a bluish-white flame, and forming bismuth trioxide, Bi_2O_3 . Chlorine and nitric acid attack it readily, but hydrochloric and sulphuric acids, when cold, have no action upon it.

Bismuth is used in the arts chiefly for forming alloys. *Rose's fusible metal* is composed of 1 part of lead, 1 of tin, and 2 of bismuth; it melts at 94° C. *Lipowitz's fusible metal* contains 3 parts of cadmium, 4 of tin, 8 of lead, and 15 of bismuth; it melts at 60° C. An alloy of lead and bismuth is used in the so-called *permanent metallic pencils*. Bismuth is also employed in medicine. (U. S. P., pages 78 to 84, inclusive, and 260 to 261.)

OXIDES AND ACIDS OF BISMUTH

107. There are four oxides of bismuth, and one hydrate that has the form of metarsenic and metantimonic acids, and is generally called *bismuthic acid*. These compounds have basic rather than acidic properties, showing that bismuth should be considered as a base-forming element. Though its metallic characteristics appear to predominate, its general

chemical relations place it in this group. The oxides and acid are as follows:

OXIDES	ACID
Bismuth dioxide, Bi_2O_2	Bismuthic acid, $HBiO_3$
Bismuth trioxide, Bi_2O_3	
Bismuth tetroxide, Bi_2O_4	
Bismuth pentoxide, Bi_2O_5	

108. Bismuth dioxide, Bi_2O_2 , may be obtained by adding potassium hydrate to a mixture of bismuth trichloride and stannous chloride. As stannous chloride tends to change to stannic chloride, it acts as a reducing agent, and probably takes some of the chlorine from the bismuth trichloride, forming a compound of the composition $BiCl_2$. The potassium hydrate, acting on this, precipitates bismuth dioxide, Bi_2O_2 , in the form of a brown precipitate. It is obtained also by heating metallic bismuth in the air. It is a citron-yellow powder, stable in the air, and is insoluble in water and in the alkalies.

109. Bismuth trioxide, Bi_2O_3 , is the principal oxide of bismuth and is formed when bismuth is burned in air or oxygen. It may also be prepared by igniting the nitrate, $Bi(NO_3)_3$, at a high temperature. It is a yellow powder, with basic properties. *Bismuth tetroxide*, Bi_2O_4 , is a reddish-yellow powder of which little is known.

110. When chlorine is led through a concentrated solution of potassium hydrate in which bismuth trioxide is suspended, bismuthic acid, $HBiO_3$, is precipitated; this, when gently heated, yields **bismuth pentoxide**, Bi_2O_5 . Some experimenters claim to have obtained salts of bismuthic acid, such, for example, as $NaBiO_3$, while others have failed. At all events, the acid properties of bismuthic acid, and of the pentoxide, are very weak.

111. Bismuthic acid, $HBiO_3$, as stated above, is obtained by passing chlorine through a concentrated solution of potassium hydrate, in which bismuth trioxide is suspended. It may act as a very weak acid toward strong bases, but its general character is rather basic. It is a scarlet-red powder which at 120° C. gives up its water, forming the pentoxide.

BISMUTH AND CHLORINE

112. Bismuth forms two compounds with chlorine, namely: $BiCl_3$ and $BiCl_2$. The trichloride is the principal one. It may be formed by the direct action of chlorine on bismuth. It is a white, granular, deliquescent substance, fusible at 230° C., and volatile at 435° C. By contact with water it is decomposed, forming **bismuthyl chloride**, $BiOCl$, also known as *bismuth oxychloride*.

The trifluoride, tribromide, and tri-iodide are similarly prepared, and in presence of water these yield precipitates of basic salts.

BISMUTH AND SULPHUR

113. **Bismuth trisulphide**, Bi_2S_3 , occurs in nature as bismuthinite. It is obtained as a black precipitate on adding hydrogen sulphide to solutions of bismuth; but, unlike the sulphides of arsenic and antimony, it is not soluble in solutions of the alkali sulphides. Salts called *sulphobismuthites* are formed when combination takes place between Bi_2S_3 and a metallic sulphide. Some of these occur in nature, as, for example, lead sulphobismuthite, or *kobellite*, $Pb_3(BiS_3)_2$; sulphobismuthite of copper, or *emphelctite*, $Cu(BiS_2)_2$; *wittichenite*, $Cu(BiS_3)_2$.

SALTS OF BISMUTH

114. By treating a solution of bismuth nitrate, $Bi(NO_3)_3$, with a cold solution of potassium hydrate a precipitate of bismuth hydrate, $Bi(OH)_3$, is obtained. If this is dried at 100° C. water is driven off, and the hydrate $BiOOH$ results. The salts of bismuth are derived from these two hydrates. The salts derived from the triacid base, $Bi(OH)_3$, are known as *bismuth salts*, and those derived from the monacid base, $BiOOH$, are called *bismuthyl salts*. The most common salts of bismuth are the sulphates and nitrates. By dissolving bismuth trioxide in dilute sulphuric acid, *acid bismuth sulphate*, $BiH(SO_4)_2$, is obtained. This compound is not as stable,

however, as *bismuthyl sulphate*, $(\text{BiO})_2\text{SO}_4$. *Bismuth nitrate*, $\text{Bi}(\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$, is obtained by dissolving bismuth in nitric acid and evaporating to dryness. Water decomposes this salt, forming basic nitrates, the composition of which depends on a number of circumstances, as, for example, the quantity and temperature of the water, the amount of free acid present, etc. Among the best known basic nitrates of bismuth are: BiONO_3 , $\text{Bi}(\text{OH})_2\text{ONO}_2$, and $(\text{BiO})_2\text{OHONO}_2$.

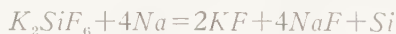
There are many others, however, that are more complex in composition.

SILICON

Symbol Si. Atomic weight 28.3. Molecular weight 28.3. Valence IV.

115. History and Occurrence.—Silicon was first obtained pure by Berzelius in 1825. It does not occur free in nature, but is found abundantly in combination with oxygen, forming such well-known substances as quartz and flint. In combination with oxygen, as well as with aluminum, potassium, and various other metals, it constitutes a large portion of the rock formations that compose the solid crust of the earth.

116. Preparation and Properties.—Silicon may be obtained by the action of sodium on potassium fluosilicate:



The silicon thus obtained is a brown powder (*amorphous silicon*) that resists the action of all acids, except hydrofluoric, by which it is decomposed forming silicon tetrafluoride and evolving hydrogen:



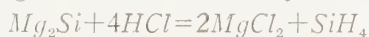
If potassium fluosilicate is fused with aluminum, a portion of the latter combines with the fluorine, while the remainder combines with the silicon, forming aluminum silicide. By boiling this with hydrochloric acid and then with hydrofluoric acid, the aluminum is extracted and crystalline scales of silicon, possessing a metallic luster, resembling that of black lead, are left. These crystalline scales are known as *graphitoid silicon*.

In this shape, silicon does not burn in oxygen, nor is it then soluble in hydrofluoric acid; a mixture of nitric and hydrofluoric acid, however, is capable of dissolving it. Though amorphous silicon is a non-conductor of electricity, the crystalline variety, like graphite, readily conducts it. The amorphous variety may, through an extremely intense heat, be transformed into the incombustible and insoluble form. It seems appropriate to remark that the combustibility of amorphous carbon (charcoal) is also diminished to a considerable extent after exposure to a high temperature.

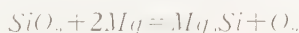
SILICON HYDRIDE

Formula SiH_4 . *Molecular weight* 32.3

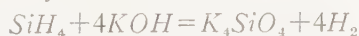
117. Preparation.—Silicon hydride may be prepared by decomposing magnesium silicide with hydrochloric acid:



The magnesium silicide may be prepared by intensely heating together powdered sand or quartz with magnesium powder; thus,



118. Properties.—Silicon hydride is a colorless gas, which at -1°C . under a pressure of 70 atmospheres is condensed into a liquid. It is insoluble in water. When mixed with hydrogen, it is spontaneously inflammable in air, yielding white clouds of silicon dioxide. Burned from a jet, the gas gives a brilliant white flame that deposits a layer of brown silicon upon a disk or plate of porcelain held in it. When the tube conveying the gas is heated, a mirror-like deposit of silicon is formed within the tube. Passed into cupric sulphate or silver nitrate, it precipitates cupric and silver silicide, respectively. Its composition can easily be proved by decomposing it with potassium hydroxide:



SILICON DIOXIDE, OR SILICA

Formula SiO_2 . Molecular weight 60.3

119. Occurrence.—The only oxide of silicon known, silicon dioxide, or silica, is found widely distributed in nature as quartz, opal, flint, sand, etc. It occurs also in combination with bases in the form of silicates, as asbestos, mica, soapstone, cement, glass, etc. Its purest form is the transparent and colorless variety known as *quartz*, which crystallizes in the hexagonal system and has a specific gravity of 2.6. When colored a delicate purple, the crystals are known as *amethysts*. When its transparency and crystalline structure are lost and it is colored with iron oxide, it becomes *chalcedony* and *carnelian*.

120. Preparation and Properties.—Silica may be prepared either by the oxidation of silicon, as when it burns in the air, or by the dehydration of silicic acid:



Silicon dioxide, in the form in which it is usually obtained, is a white amorphous powder, though in nature it frequently occurs in the form of hexagonal prisms. It has a specific gravity of 2.6, is so hard as to scratch glass, and is fusible only by means of the oxyhydrogen blowpipe. It is insoluble in water and all acids, but is soluble in the fixed alkalies, and is decomposed by hydrofluoric acid, forming silicon fluoride and water.

When a portion of the sodium hydroxide solution of silica, sodium silicate, or *water glass*, is treated with a few drops of hydrochloric acid, gelatinous silicic acid will separate out.

121. Natural crystallized silica is not soluble in boiling solutions of the alkalies, nor is it soluble in any of the acids with the exception of hydrofluoric acid. The amorphous variety, on the other hand, is readily soluble in boiling alkalies. Thus, silica is found to exist in two modifications, and is dimorphous. A crystal of quartz may be heated to a bright redness without change; but, if powdered previous to being heated its specific gravity changes from 2.6 to 2.4, and it becomes soluble

in boiling alkalies. In other words, by fine grinding and heating the crystalline modification becomes converted into the amorphous.

By far the greatest number of minerals are silicates. Clays are aluminum silicates, meerschaum and talc are silicates of magnesium, feldspar is a silicate of aluminum and potassium, the various glasses are silicates of sodium, potassium, lead, calcium, etc. The majority of the silicates are represented as derivatives of metasilicic acid and polysilicic acids of the general formula $nH_2O \cdot SiO_2$.

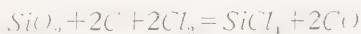
122. Uses of Silica.—Silica is largely employed in all its various forms. Rock crystal is used for the manufacture of ornaments, etc. Chalcedony, onyx, and opal are sought for by the engraver and lapidary. Agate, which is very hard, is used for the manufacture of mortars, etc. Sandstone serves for building purposes and for grindstones; sand, for mortars, the manufacture of glass, pottery, etc.

Fused silica ware, either transparent or opaque, is now largely used in commercial laboratories, in the form of crucibles, evaporating dishes, and tubes. It has a great physical advantage over porcelain ware, in that it may be heated to a red heat and immersed in water, if necessary, without cracking it; in other words, it withstands extreme and sudden temperature changes. (U. S. P., pages 437 and 439.)

SILICON TETRACHLORIDE

Formula $SiCl_4$. Molecular weight 170.14

123. Preparation and Properties.—Silicon tetrachloride is formed when silicon is heated to dull redness in a current of chlorine, or when the latter gas is passed over an incandescent mixture of charcoal and silica, according to the equation:



Silica, lampblack, and oil are thoroughly mixed into a stiff paste, which is made into little balls that are placed in a crucible, the cover of which is then luted, and the whole is heated

distils over and condenses in globules, still containing carbon in the form of charcoal. It is purified by redistillation in an iron retort, and is condensed in a copper receiver filled with naphtha.

Potassium may also be prepared by the electrolytic methods described under the preparation of metallic sodium.

3. Properties.—Potassium is a soft, brilliant, bluish-white metal, tarnishing instantly, however, in the air to a dull, grayish color. It must always be preserved under naphtha. It possesses a specific gravity of .875, becomes brittle at 0° C., and melts at 62.5° C. to a liquid closely resembling mercury.

If thrown on water, potassium at once decomposes it, thereby evolving so much heat that the hydrogen, set free, takes fire and burns with a characteristic violet flame. It unites actively with chlorine and with sulphur.

POTASSIUM OXIDES

4. Potassium Oxide, K_2O .—Potassium oxide is obtained by the direct oxidation of the metal, as when it is burned in air or oxygen and the product is ignited, or when potassium hydroxide is heated with potassium, according to the equation:

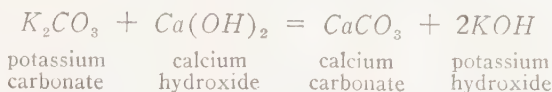


It is a grayish-white, deliquescent, caustic substance, and unites energetically with water to again form the hydroxide.

5. Potassium Peroxide, or Tetroxide, K_2O_4 .—Potassium peroxide is formed when potassium is heated with an excess of oxygen. It is a yellow powder which at white heat breaks up into potassium oxide and oxygen. On treatment with water, potassium hydroxide and hydrogen peroxide are formed and oxygen is set free. It is a strong oxidizing agent.

6. Potassium Hydroxide, or Caustic Potash, KOH . Potassium hydroxide is also called caustic potash and, *incorrectly*, potassium hydrate. It may be prepared by adding *milk*

of lime, or slaked lime, $Ca(OH)_2$, to a dilute boiling solution of potassium carbonate. Thus,



When the reaction has gone to completion, determined by testing a portion of the clear solution with HCl , absence of effervescence indicating completion, the liquid is allowed to settle, and the clear solution is decanted and rapidly evaporated. The residue is melted in a silver dish and poured out on flat stone slabs. This product is impure, and by treating it with alcohol, which dissolves only the potassium hydroxide, it may be freed of lime and any salts of potassium it may possess—especially of the carbonate, which is formed by the absorption of carbon dioxide from the air during evaporation. The clear alcohol solution is decanted, and after the alcohol has been expelled by distillation, the residue is evaporated to dryness and fused in a silver dish.

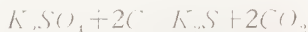
7. Potassium hydroxide is frequently prepared also by the electrolysis of a solution of potassium chloride.

Recently fused potassium hydroxide occurs as opaque, white fragments having a short fibrous fracture. It melts just below a red heat to an oily liquid, and volatilizes at a white heat; it is not decomposed by heat. When exposed to the air, it absorbs moisture as well as carbon dioxide from the atmosphere, and deliquesces. It is very soluble in water.

Potassium hydroxide is very caustic; it softens and partly destroys the skin, and is, for this reason, employed as a caustic in surgery. It shows the properties of an alkali in the highest degree; these are, its solubility in water, its power to neutralize the acids and to decompose a great number of metallic solutions, and its corrosive action on the tissues. This alkalinity may be shown by the energy with which the most dilute solutions of potassium hydroxide restore the blue color to reddened litmus. (U. S. P., page 252.)

SULPHIDES OF POTASSIUM

8. Potassium Sulphide, K_2S .—Potassium sulphide is obtained by passing hydrogen over heated potassium sulphate, or by gently heating a mixture of potassium sulphate and carbon; thus:

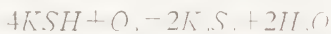


The sulphide obtained by using hydrogen is a red, crystalline mass, whereas a flesh-colored porous mass is obtained when carbon is used. A solution of the sulphide can be obtained by saturating a solution of potassium hydrate with hydrogen sulphide and adding an equal quantity of the hydrate. If the sulphide is fused it solidifies in a red, crystalline mass, which is deliquescent in moist air and is soluble in water. (U. S. P., page 330.)

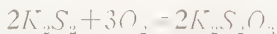
9. Potassium Hydrosulphide, KSH .—Potassium hydrosulphide may be prepared by treating potassium carbonate heated to dull redness with hydrogen sulphide, as shown in the equation:



It forms a white or yellow deliquescent solid, very soluble in water. Exposed to the air its aqueous solution becomes yellow from the formation of the disulphide; thus:



If exposed for a longer time, the solution becomes colorless, potassium thiosulphate being formed; thus:



POTASSIUM AND CHLORINE

10. Potassium Chloride, KCl .—Potassium chloride constitutes the mineral *sylvite*, and closely resembles rock salt. It is obtained commercially from sea-water, from kelp (the ash of seaweed), from the refuse of the manufacture of sugar from beet root, or from an abundant mineral of the Stassfurt mines, *carnallite*, which is potassium-magnesium chloride. It is a transparent, colorless solid that crystallizes in cubes; it has

a specific gravity of 1.98 and a bitter, salty taste. It is soluble in water and produces a depression of temperature in dissolving.

POTASSIUM AND IODINE

11. Potassium Iodide and Bromide.—*Potassium iodide* and *bromide* are commercially important on account of their use in medicine and photography.

Potassium iodide, KI , is prepared on a large scale by the direct action of iodine on potassium hydroxide:



Potassium iodide and iodate are formed, the latter being precipitated. The whole is evaporated to dryness, and the residue heated to redness with powdered charcoal, whereby the iodate is converted into iodide. The mass is dissolved in hot water; on cooling, the solution deposits the iodide in fine, colorless, transparent cubes. One hundred parts of water at 18° C. dissolves 143 parts of potassium iodide; it is also readily soluble in alcohol. A solution of potassium iodide dissolves iodine readily. (U. S. P., pages 340, 341, and 545.)

Potassium bromide, KBr , is similar in properties to the iodide and is obtained by an analogous process. It crystallizes in cubes that are soluble in about 1.5 parts of cold water.

SALTS OF POTASSIUM

12. Potassium Nitrate, KNO_3 .—Potassium nitrate, long known as **saltpeter**, or **niter**, is found in some parts of India, in Egypt, Persia, Hungary, Spain, etc., where it sometimes appears as a white incrustation on the surface of the soil and is sometimes mixed with the soil to some depth. The saltpeter is extracted from the earth by treating the earth with water; the solution formed is evaporated, at first by the heat of the sun and afterwards by artificial heat, when the impure crystals are obtained, which are exported as *grough* (or impure) *saltpeter*. It is far less abundant in northern climates

than in southern. It is formed wherever nitrogenized organic substances decompose in the presence of potassium hydroxide, and is manufactured, artificially, by exposing to the air mixtures of animal matters with wood ashes and lime, moistened with stable drainings or stale urine. The greater part of the saltpeter of commerce is now obtained from sodium nitrate, of which enormous deposits occur in Peru and Chile.

The conversion of this so-called *Chile saltpeter* into potassium nitrate is effected in the following manner: The recrystallized sodium nitrate is dissolved in water, and an equivalent quantity of potassium chloride, which is abundantly obtained from the Stassfurt mines, is added, when a double decomposition takes place. The solution is boiled down; the hot liquid deposits sodium chloride, which is separated, and potassium nitrate crystallizes out on cooling.

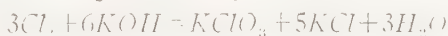
Potassium nitrate crystallizes from its aqueous solution in long, six-sided prisms that have a cool and slightly bitter taste. It melts at 340° C.; at a higher temperature it disengages oxygen and is converted into *potassium nitrite*, KNO_2 , which in its turn is decomposed at a red heat, leaving a mixture of oxide and peroxide of potassium. Potassium nitrate is very soluble in water, the solvent power of the water increasing as its temperature rises. While 100 parts of water at 0° C. dissolves only 13.33, at 100° C. it dissolves 246 parts. Potassium nitrate is largely used in the manufacture of gunpowder, which is an intimate mixture of niter, charcoal, and sulphur. (U. S. P., pages 341 and 545.)

13. Potassium Sulphate, K_2SO_4 .—Potassium sulphate may be obtained by saturating, with potassium carbonate, the acid potassium sulphate that is formed in the preparation of nitric acid by the decomposition of potassium nitrate with sulphuric acid. It is prepared also by the action of concentrated sulphuric acid on potassium chloride. Potassium sulphate melts at $1,050^{\circ}$ C., is soluble in about 10 parts of cold water, but in a much smaller quantity of boiling water; it has a bitter taste and is neutral to test paper. Its crystals are a combination of rhombic pyramids and prisms, resembling those of

quartz in formation and appearance; they are anhydrous and decrepitate when suddenly heated, which is often the case with anhydrous crystals, that is, those that contain no water of crystallization. They are insoluble in alcohol. (U. S. P., pages 545 and 546.)

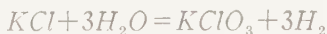
14. Acid Potassium Sulphate, $KHSO_4$.—Acid potassium sulphate, commonly known as *potassium bisulphate*, may be prepared by mixing potassium sulphate with half its weight of concentrated sulphuric acid, and evaporating the mixture to dryness in a platinum vessel; the fused salt thus obtained is then dissolved in hot water and left to crystallize. The crystals melt at about 200°C. , losing water and being converted into the pyrosulphate, $K_2S_2O_7$. They are much more soluble than the normal salt, requiring only twice their weight of water having a temperature of 15.5°C. and half that quantity at 100°C. ; the solution is acid and has a sour taste.

15. Potassium Chlorate, $KClO_3$.—Potassium chlorate may be prepared by passing chlorine into a hot (70°C.), aqueous solution of potassium hydroxide; thus,



(See *Inorganic Chemistry for Pharmacy Students*, Part 3.)

At present, however, it is also made by an electrolytic process. Hot solutions of potassium chloride are electrolyzed; the intermediate steps of the reaction which takes place are in doubt, but chlorine is first formed, then potassium hypochlorite, and finally potassium chlorate. The reaction may be summed up as follows:



Potassium chlorate melts at 357°C. , and at a higher temperature is decomposed into oxygen, potassium perchlorate, and potassium chloride. Potassium chlorate deflagrates when thrown upon hot coals; when mixed with sulphur, it explodes by friction or percussion. It is a powerful oxidizing agent. (U. S. P., pages 335 and 474.)

16. Potassium Carbonate, K_2CO_3 .—Potassium carbonate is met in commerce in the impure condition, under the name **potash**. It is obtained by *lixiviating* wood ashes; that

is, digesting them with water, evaporating the solution to dryness, and calcining the residue in the air. The potash thus obtained is impure potassium carbonate, mixed with various other salts of potassium, such as the chloride and sulphate and silicate, and only contains, approximately, from 60 to 80 per cent. of carbonate. Potassium carbonate is now manufactured on a large scale from the native chloride, so-called *Stassfurt salt*, by a similar process to that described for the manufacture of sodium carbonate from common salt.

17. Pure potassium carbonate forms a white granular powder or a white solid mass very soluble in water; it has a strong alkaline reaction, and a slightly caustic taste. It is insoluble in alcohol. It melts at 909° C., and volatilizes at a white heat. It absorbs moisture readily from the air. Potassium carbonate is largely employed for various purposes in the arts, and is a compound of considerable importance. (U. S. P., pages 334 and 544.)

18. **Acid Potassium Carbonate**, $KHCO_3$.—Acid potassium carbonate, or **potassium bicarbonate**, being much less soluble than the normal salt, crystallizes out of solution when a concentrated solution of the normal salt is treated with carbon dioxide; thus:

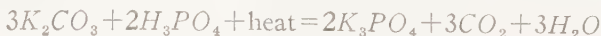


It is prepared also by passing carbon dioxide over moist potassium carbonate and recrystallizing the product from warm water. It crystallizes in large transparent monoclinic prisms, without water of crystallization. It has a salty taste and an alkaline reaction. Heated to 190° C., or by boiling the aqueous solution, carbon dioxide is evolved and water is given off with the formation of the normal salt according to the equation:



(U. S. P., pages 331 and 332)

19. **Potassium Phosphates.**—*Potassium orthophosphate*, K_3PO_4 , is formed by igniting phosphoric acid with excess of potassium carbonate. Thus,



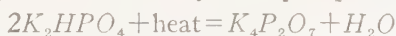
It is readily soluble in water and crystallizes in small needles. The secondary salt, K_2HPO_4 , is obtained by mixing aqueous phosphoric acid with a quantity of carbonate of potassium sufficient to produce a slight alkaline reaction, and evaporating. This salt is easily soluble in water, but it does not crystallize. The reaction is as follows:



The primary salt, KH_2PO_4 , obtained by using a slight excess of phosphoric acid, forms small needle-shaped crystals, which are easily soluble in water, but insoluble in alcohol. It is used in artificial fertilizers. The reaction between the carbonate and the acid is as follows:



Potassium pyrophosphate, $K_4P_2O_7$, is deliquescent and separates from aqueous solution in fibrous crystals. It is formed by the heating of the secondary orthophosphate.

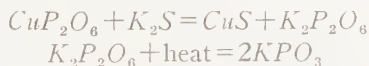


The acid salt, $K_2H_2P_2O_7$, separates as a deliquescent mass on adding alcohol to a solution of the normal pyrophosphate in acetic acid.

Potassium metaphosphate, KPO_3 , is formed by heating the primary phosphate,



This salt is almost insoluble in water; the dimetaphosphate, $K_2P_2O_6 \cdot H_2O$, prepared by decomposing the corresponding copper salt with potassium sulphide, is soluble in water and crystallizable; it is converted by ignition into the monometaphosphate. Thus,



20. Potassium Arsenates.—The *neutral salt*, K_3AsO_4 , is obtained by treating arsenic acid with an excess of potassium carbonate. The secondary salt, K_2HASO_4 , is crystallized with difficulty. The primary salt, KH_2AsO_4 , forms large crystals.

21. Potassium Arsenites.—The salt, $KH_3As_2O_5$, is obtained as a crystalline powder on adding alcohol to a solu-

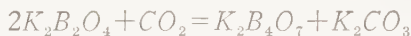
tion of arsenious oxide in the minimum quantity of potassium carbonate. When heated with a solution of potassium carbonate, it is converted into the meta-arsenite, $KAsO_2$; thus,



This salt, in turn, when heated with potassium hydroxide, yields the *diarsenite*, $K_4As_2O_5$.

A solution of potassium arsenite, known in medicine as *Fowler's solution*, is prepared by boiling 1 part of arsenious oxide with 1 part of potassium carbonate in distilled water, and diluting to 90 parts of solution. (U. S. P., page 251.)

22. Potassium Borates.—The *metaborate*, $K_2B_2O_4$, is obtained by fusing a mixture of boric acid and potassium carbonate; it is only slightly soluble in water and separates in small monoclinic crystals. It has an alkaline reaction and absorbs carbon dioxide from the air, being thereby converted into the *pyroborate* or *tetraborate*, $K_2B_4O_7$. Thus,



This latter, which is also formed on mixing a solution of boric acid with a slight excess of potassium carbonate, is easily soluble, and crystallizes in hexagonal prisms containing $5H_2O$.

The *triborate*, $2KB_3O_5 \cdot 5H_2O$, is formed on mixing the hot solution of boric acid and potassium carbonate, and separates in glittering rhombic crystals.

23. Potassium Silicate.—A silicate of potassium is formed when silica is fused with potassium carbonate. Its composition appears to vary. It is soluble in water, and on evaporating in air the solution deposits a glassy-appearing substance. For this reason it is called *water glass*. It may be prepared also by dissolving silicon dioxide in potassium hydroxide.

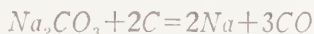
SODIUM

Symbol Na. Atomic weight 23.0. Molecular weight 23.0. Valence I.

24. History and Occurrence.—Though sodium oxide was already recognized in the year 1736 by Duhamel, the metal

in the pure state was only obtained in 1807 by Sir Humphry Davy. Sodium does not occur in the free state in nature, but is found abundantly in combinations. Its chloride, or salt, is known as the mineral *halite*, and is found not only in immense deposits of rock salt but also in enormous quantities in sea-water and in the waters of saline springs. Sodium also occurs in the form of nitrate, or Chile saltpeter; of borate, or borax; of carbonate, or trona; and of silicate, in albite, oligoclase, sodalite, etc. It is found in marine plants, and is essential to animal life.

25. Preparation and Properties.—Sodium may be prepared by distilling a mixture of sodium carbonate and carbon, when the metal distils over, according to the equation:



To purify it, it was formerly distilled, melted under petrol-eum, and cast into ingots, which had to be preserved under kerosene or some similar substance free from water. This process has been almost entirely superseded by an electrolytic method—the electrolysis of the hydroxide. In this method fused sodium hydroxide is electrolyzed in an iron vessel. The metallic sodium, being lighter than the hydroxide, rises, together with the hydrogen, from the negative pole and is collected in a receiver. The hydrogen escapes around the edges of the cover of the receiver and the sodium is skimmed off. More sodium hydroxide is added from time to time to replace the metal removed, thus making the process continuous.

Sodium is a lustrous, silver-white, soft metal; its specific gravity is .972; it becomes brittle at -20° C., melts at 97.6° C., and boils at 877.5° C. On exposure to air it rapidly tarnishes, and if thrown on water, decomposes it with effervescence; if it is prevented from moving or if the water is warm, it takes fire, burning with a characteristic yellow flame. Sodium is far less costly than potassium, and is used on a large scale for the extraction of the metal magnesium and for making sodium peroxide. An amalgam of sodium is also employed with advantage in extracting gold and silver from their ores.

COMPOUNDS OF SODIUM

26. Sodium Chloride.—Sodium chloride, NaCl , is common salt, or sea salt. It is widely diffused in nature and is found in the solid state, as rock salt, in many countries. Sea-water contains a large proportion of sodium chloride, and it exists also in various mineral springs. It may be formed by the direct union of its constituents, as by burning sodium in chlorine gas. It is obtained commercially either by mining it directly, in which form it is known as rock salt, or by evaporating either sea-water or the waters of saline springs, producing solar salt if the heat is natural, and boiled salt if artificial heat is employed.

Extensive beds of rock salt occur in Russia, France, Germany, Hungary, Spain, Abyssinia, Mexico, and various parts of the United States. Perfectly pure specimens of rock salt form beautiful, colorless cubes, and are known as *sal gemme*, but ordinary rock salt is only partly transparent and exhibits a rusty color, owing to the presence of iron.

27. Sodium chloride is a colorless, transparent solid that crystallizes from its aqueous solution in cubes. The crystals are generally very small, are anhydrous, and nearly equally soluble in hot and cold water.

The great tendency of ordinary table salt to become damp when exposed to the air is due chiefly to the presence of small quantities of chlorides of magnesium and calcium, which slowly absorb moisture from the air; pure sodium chloride has very little tendency to attract atmospheric moisture, although it is easily dissolved by water.

Salt is used as a refrigerating medium and for preserving meats, fish, etc.; it is also used in the manufacture of soaps and pottery, and salt solutions are employed in surgery. (U. S. P., page 387.)

28. Oxides of Sodium.—*Sodium oxide*, Na_2O , may be obtained by the combustion of sodium in air and heating the product with sodium; it is a white, fusible substance, uniting directly with water to form *sodium hydroxide*, NaOH .

Sodium peroxide, Na_2O_2 , is produced on a commercial scale by heating sodium to 300°C . in a current of dry air. It is a yellowish substance, turning white on exposure to air, and acts as a powerful oxidizing agent. Water decomposes it, forming sodium hydroxide and liberating oxygen. It is largely applied in bleaching silk and wool.

Sodium hydroxide, NaOH , generally known as *caustic soda*, is frequently employed in the laboratory and in the arts. It is prepared, in the pure state, by the action of the metal on water; commercially, it is obtained by the action of calcium hydroxide—milk of lime—on sodium carbonate. (See *Potassium Hydroxide*.)

Sodium hydroxide is deliquescent, freely soluble in water, and absorbs carbon dioxide from the air. For laboratory use

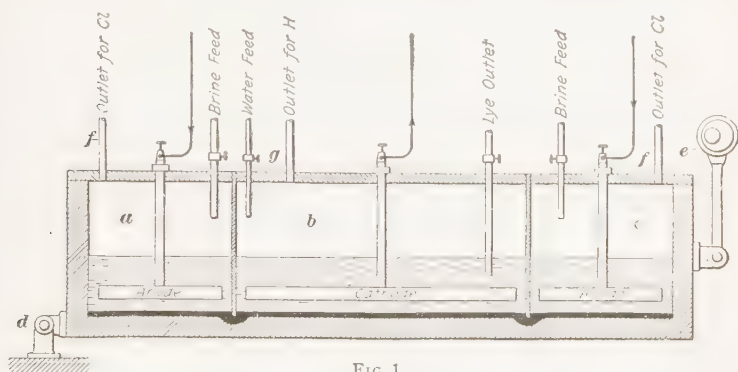


FIG. 1

it usually comes to the market in the form of small sticks, while for commercial purposes it is either sold in solutions of given strengths or the fused product is run into large drums or steel containers. (U. S. P., page 390.)

29. The Castner-Kellner Process.—Many methods have been suggested for the commercial production of chlorine by the electrolysis of a solution of common salt. One of the oldest and most generally used is the Castner-Kellner process, which is worked in this country on a large scale.

Fig. 1 is a diagram that shows the general disposition, but not the relative sizes, of the active parts and material. The

box is constructed of a non-conducting material, such as slate, and is about 4 feet long, 4 feet wide, and 6 inches deep. It is divided into the compartments *a*, *b*, and *c* by means of partitions that extend to within $\frac{1}{16}$ inch from the bottom. As the bottom is covered with a layer of mercury, about $\frac{1}{8}$ inch thick, it follows that each compartment is separated from the adjoining one.

A nearly saturated solution of NaCl , or brine, is supplied to each of the compartments *a* and *c*, the compartment *b* containing pure water. Carbon anodes are employed and a cathode consisting of an iron grid. The box is pivoted at *d*, the other end being supported by an eccentric rod connecting with an eccentric *e*, which makes one revolution per minute and raises and lowers that end through a height of $\frac{1}{2}$ inch. This rocking motion causes the mercury to flow backward and forward between the compartments.

30. As the current passes from the anodes into the solution contained in the compartments *a* and *c*, chlorine is liberated at the anode and removed by suction through the pipes *f, f*. Those portions of the mercury layer that extend into the cells *a* and *c* must be considered as intermediate cathodes. Hence, sodium is liberated at the mercury surface in these cells, the sodium alloying itself with the mercury. The rocking of the box causes the sodium-mercury alloy to pass into the compartment *b*, where the sodium at once combines with the water and forms caustic soda and hydrogen, the latter escaping through the pipe *g*. Suitable arrangements are made for a constant supply of a concentrated salt solution to cells *a* and *c*, and a withdrawal of the lye solution from the cell *b*. This solution is evaporated and sold in one of the commercial forms of sodium hydroxide, or the solution of sodium hydroxide is converted into sodium carbonate, Na_2CO_3 .

It is important to note that a portion, amounting to 10 per cent., of the electric current entering through the anodes must be shunted off before it reaches the cathode; this is to prevent the mercury from passing into solution in the compartment *b* and forming HgO , thus not alone causing a serious loss of

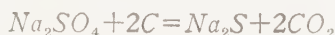
this metal, but also destroying its metallic continuity. The current strength at each anode is about 630 amperes and the pressure 4.3 volts. The apparatus decomposes nearly 130 pounds of sodium chloride during a period of 24 hours, giving about 80 pounds of chlorine and 88 pounds of sodium hydroxide.

31. Sodium Carbonate.—Sodium carbonate, Na_2CO_3 , one of the most widely used salts, generally known as *soda*, or *soda ash*, is obtained on a very large scale by a number of methods. One of the oldest methods is that of Le Blanc.

32. In the **Le Blanc process** salt and sulphuric acid are heated together, when the change shown in the following equation takes place:



The sodium sulphate, or *salt cake*, thus obtained is mixed with coal and limestone and again heated, when the sodium sulphate is converted into the carbonate in two steps represented by the equations:



and

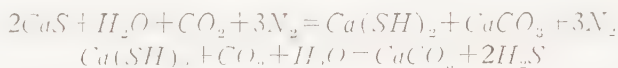


The mixture of sodium carbonate and calcium sulphide, known as *black ash*, is leached with water, dissolving the soluble sodium carbonate from the insoluble calcium sulphide. The solution is then evaporated, when the sodium carbonate crystallizes.

In this process the salt and sulphuric acid are charged into the pan *A*, Fig. 2, and are heated by the fire on the grate *C*, the door *F* remaining closed. Large quantities of hydrochloric acid gas are evolved and these pass through the flue *B* to a brick tower, where they are condensed. The door *F* is now raised and the partly decomposed salt is transferred to the muffle part *D* of the furnace, where the decomposition is completed. The hydrochloric acid gas evolved here passes to the condensing towers through the flue *E*.

For about each ton of soda ash produced there is about $1\frac{1}{2}$ tons of waste. This is recovered by pumping the carbon

dioxide, evolved in the burning of the coal and limestone, into tall closed cylinders which contain the waste mixed to a creamy consistency with water. The carbon dioxide first forms calcium hydrosulphide, calcium carbonate, and nitrogen. The calcium hydrosulphide is then converted into the carbonate with an evolution of hydrogen sulphide. These two steps are represented by the equations :



The hydrogen sulphide is then burned and produces sulphur and water.

33. The **Solvay process**, or the *ammonia-soda process*, has to a large extent superseded the Le Blanc process. This

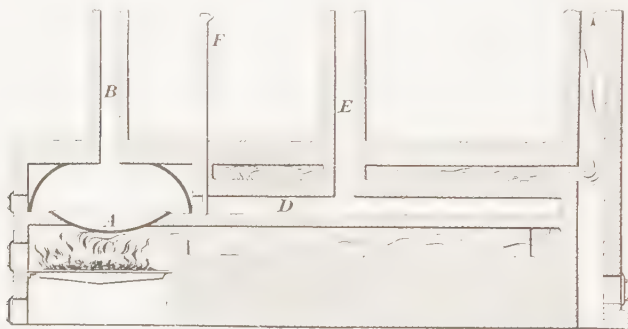
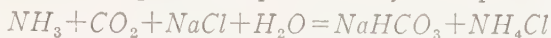


FIG. 2

process depends on the double decomposition that occurs when carbon dioxide is passed into a solution of sodium chloride containing ammonia. This process yields a purer product than the Le Blanc process, is less expensive, and gives rise to no noxious by-products.

Brine obtained either directly from the mines or by dissolving rock salt is purified by treatment with calcium hydroxide, which removes the magnesium salt. The calcium salts are then removed by either sodium carbonate or weak solutions of ammonium carbonate, after which the brine is saturated with ammonia. The ammoniacal brine is forced into tall towers and

carbon dioxide is forced in at the bottom of the towers. The reaction that takes place is represented by the equation:



The sodium bicarbonate, in the form of a pasty liquid, is drawn off, washed, dried, and calcined, thus driving off the ammonium salts and converting the bicarbonate into the neutral carbonate; thus:



The carbon dioxide driven off is again utilized by being absorbed by fresh brine.

34. Sodium carbonate crystallizes, at ordinary temperatures, with 10 molecules of water of crystallization in large monoclinic prisms that effloresce in the air and crumble to a white powder. It has an alkaline taste, and melts at 849° C. It is soluble in water, the solution having a strong alkaline reaction. (U. S. P., page 386.)

35. Acid Sodium Carbonate.—Acid sodium carbonate, *sodium bicarbonate*, or *bicarbonate of soda*, $NaHCO_3$, is prepared by the action of carbon dioxide on the normal carbonate. It forms small monoclinic tabular crystals, or a white crystalline powder. It is less soluble in water than the normal carbonate, and the solution is much less alkaline. When boiled, its solution evolves carbon dioxide. The salt itself readily decomposes, when gently heated, into sodium carbonate, carbon dioxide, and water. (U. S. P., page 383.)

36. Sodium Sulphate.—Sodium sulphate, Na_2SO_4 , or *salt cake*, is obtained abundantly, commercially, as a residue in various chemical processes, as, for instance, in the preparation of nitric and hydrochloric acids. It is also largely produced as an intermediate product in the manufacture of soda. It occurs in nature, anhydrous as *thenardite*, and hydrated as *mirabilite*. It crystallizes from solution in large, colorless prisms that have the composition $Na_2SO_4 \cdot 10H_2O$ and are efflorescent in dry air, losing all their water. This is *Glauber's salt*. (U. S. P., page 398.)

37. Acid Sodium Sulphate.—Acid sodium sulphate, NaHSO_4 , is obtained by adding sulphuric acid to the neutral sulphate. On cooling the saturated solution, oblique rhombic prisms are obtained, which contain 2 molecules of water of crystallization. These crystals are very readily soluble in water, and have an acid taste. Alcohol decomposes them into sulphuric acid and neutral sulphate, which latter is precipitated.

38. Sodium Sulphide and Hydrosulphide.—*Sodium sulphide*, Na_2S , may be obtained by reducing sodium sulphate. This may be accomplished by heating a mixture of sodium sulphate and carbon, or by heating the sulphate in a current of hydrogen.

Sodium hydrosulphide is prepared by the action of hydrogen sulphide on a solution of sodium hydroxide, according to the equation:



39. Phosphates of Sodium.—Three phosphates of sodium are obtained from tri-basic phosphoric acid, H_3PO_4 ; they are:

Sodium di-hydrogen phosphate, or mono-sodium phosphate, $\text{H}_2\text{NaPO}_4 \cdot \text{H}_2\text{O}$.

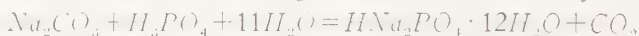
Di-sodium phosphate, $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$. (U. S. P., pages 395 and 397.)

Normal, or ortho-sodium, phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$.

Sodium di-hydrogen phosphate, $\text{H}_2\text{NaPO}_4 \cdot \text{H}_2\text{O}$, is made by adding phosphoric acid to an aqueous solution of di-sodium phosphate,



Di-sodium phosphate, $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$, is made by adding sodium carbonate to phosphoric acid until the solution is just alkaline, and then evaporating the solution until it crystallizes,



This is the ordinary sodium phosphate used in laboratories for the determination of magnesium. (U. S. P., pages 395 and 397.)

Normal, or *ortho-sodium, phosphate*, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, is made by evaporating a mixed solution of sodium hydroxide and di-sodium phosphate until crystals are obtained,



The water solution of this salt gives an alkaline reaction, which may be due to the reaction,



Meta-sodium phosphate, NaPO_3 , is made by heating sodium di-hydrogen phosphate to 204°C . or higher, the salt losing two molecules of water.



40. Sodium Borate.—Sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$, better known as *borax*, occurs as a deposit from evaporation of the waters of certain lakes in Thibet and in the United States.

When a concentrated boiling solution of borax is allowed to cool to 60°C ., it deposits octahedral crystals containing 5 molecules of water, while below 60°C . it crystallizes in monoclinic prisms containing 10 molecules of water. This latter is the familiar form of commerce. It is somewhat soluble in water, its solution is faintly alkaline, and the crystals effloresce in the air, becoming opaque.

Borax glass is obtained by fusing the crystalline borax, which swells to a white spongy mass of many times its original volume; this mass afterwards fuses to a clear, glassy mass. It dissolves many metallic oxides very easily, and these impart their own peculiar color to the glass. It finds wide employment in blowpipe analysis and in the metallurgical arts. It is antiseptic and is sometimes used as a preservative. (U. S. P., page 394.)

41. Sodium Nitrate.—Sodium nitrate, NaNO_3 , or Chile saltpeter, is found in large quantities in Peru and Chile. It crystallizes in large rhombohedra very similar to cubes; hence, it is frequently called cubic niter, to distinguish it from the prismatic potassium niter. It is used as a fertilizer, and for the manufacture of nitric acid and potassium nitrate.

AMMONIUM

Formula NH_4 . *Molecular weight* 18.04. *Valence* I

42. History.—The salts that ammonia forms by direct union show a great similarity to those formed by the metals potassium and sodium. To account for this remarkable similarity, Berzelius, in 1816, basing his ideas on a theory of Ampère, proposed to consider these salts as compounds of ammonium, NH_4 , a compound radical, capable of acting like the monad metals sodium and potassium. Being an unsaturated compound, ammonium, if it exists free, must have the formula $H_4\equiv N-N\equiv H_4$, or, in other words, must exist as a double molecule with the formula N_2H_8 . Weyl, by condensing ammonia gas in the presence of sodium, obtained a bright-blue, metallic-like liquid, which he assumed to be *sodammonium* and to which he ascribed the formula $N_2H_6Na_2$. By allowing it to act on ammonium chloride, a similar blue liquid was obtained, which is considered to be free ammonium. Moreover, when mercury containing 1 per cent. of sodium is placed in a saturated solution of ammonium chloride, it increases considerably in bulk, becoming a pasty mass, which is the so-called *ammonium amalgam*.

43. Ammonium Nitrate.—Ammonium nitrate, NH_4NO_3 , is prepared by neutralizing nitric acid with ammonia. It crystallizes in large, transparent prisms melting at $158^\circ C$., it is very soluble in water, alcohol, and liquid ammonia, and produces a notable depression of temperature in the act of solution. Heated gently, it decomposes into nitrous oxide and water. It is used largely for the manufacture of nitrous oxide (*laughing gas*), for the preparation of freezing mixtures, and for explosives. (U. S. P., page 523.)

44. Ammonium Nitrite.—Ammonium nitrite, NH_4NO_2 , forms colorless deliquescent crystals. Its solution decomposes, on heating, into nitrogen and water, as does the salt itself. A mixture of ammonium nitrite and potassium chloride is used for preparing nitrogen.

45. Ammonium Carbonate.—Ammonium carbonate, $(NH_4)_2CO_3$, is obtained when ammonia gas is passed through a solution of commercial ammonium carbonate. Exposed to the air, it gives off ammonia and becomes the bicarbonate. (U. S. P., page 44.)

46. Ammonium Bicarbonate.—Ammonium bicarbonate, $(NH_4)HCO_3$, is formed when ammonium hydroxide is saturated with carbon dioxide. It forms a white, odorless powder, slightly soluble in water, and having a salty taste. Its aqueous solution slowly decomposes into the normal carbonate with the evolution of carbon dioxide.

47. Ammonium Sulphate.—Ammonium sulphate, $(NH_4)_2SO_4$, is obtained in the arts by passing the ammonia, which is disengaged when gas liquor is heated with lime, into dilute sulphuric acid. It crystallizes in right rhombic prisms, is colorless, and has a sharp taste. It is insoluble in alcohol. It is manufactured on an extensive scale, and is used as a fertilizer and for the manufacture of other ammonium salts. (U. S. P., page 523.)

48. Ammonium Chloride.—Ammonium chloride, NH_4Cl , was formerly obtained from Egypt, where it was made by subliming the soot produced by the combustion of camel's dung. It is now produced on a large scale from gas liquor, or the water condensed in the manufacture of illuminating gas from coal. This liquor is heated with lime; ammonia is disengaged and is conducted into hydrochloric acid. Ammonium chloride is obtained by simply evaporating the solution. It is then purified by sublimation in stoneware pots, which are heated in a furnace, out of which the upper parts of the pots project. The volatilized chloride condenses, and the sublimed product is known in trade as *sal ammoniac*, or *muriate of ammonia*.

It generally occurs as a white or grayish compact mass (having a crystalline fibrous structure), which is often striped with brown, owing to the presence of a little iron. At a high temperature it volatilizes without melting. (U. S. P., pages 44, 45, and 522.)

49. Ammonium Sulphide.—Ammonium sulphide, $(NH_4)_2S$, in the form of a white crystalline mass is obtained by mixing 1 part of hydrogen sulphide gas with 2 parts of ammonia gas in a vessel cooled by a mixture of salt and ice. It is readily soluble in water, and is rather unstable, decomposing at ordinary temperature into free ammonia and ammonium hydrosulphide, NH_4HS .

When strong ammonium hydrate is saturated with hydrogen sulphide at a low temperature, a colorless solution of NH_4HS results. In contact with the air this soon becomes yellow from the formation of *ammonium polysulphides*, $(NH_4)_2S_x$. This latter solution is obtained more readily by adding sulphur to the ammonium hydroxide previous to the saturation with hydrogen sulphide. (U. S. P., page 523.)

50. Ammonium Bromide and Ammonium Iodide. *Ammonium bromide*, NH_4Br , and *ammonium iodide*, NH_4I , are largely employed in photography. The former crystallizes in white cubes having a pungent, salty taste; it is volatile at a high temperature without decomposition, and is soluble in water and alcohol. The latter crystallizes in colorless cubes, which gradually become yellow and even brown from the separation of iodine. It is hygroscopic and odorless, has a sharp, saline taste, and is extremely soluble in water and alcohol. It is volatile at a high temperature with decomposition without melting. (U. S. P., page 43.)

51. Ammonium Phosphates.—The most important of the compounds of ammonium and phosphorus is the *secondary ammonium sodium phosphate*, or *microcosmic salt*, $NH_4NaHPO_4 \cdot 4H_2O$. It is prepared by mixing hot strong solutions of ammonium chloride and sodium phosphate, thus:



It forms large transparent, monoclinic crystals that are very soluble. When heated it boils violently, giving up water and ammonia, finally forming a transparent glass of sodium metaphosphate, which is used in blowpipe work for the detection of various metals.

LITHIUM

Symbol Li. Atomic weight 6.94. Valence I

52. History and Occurrence.—Lithium oxide was recognized first as a new substance by Arfvedson, a Swedish chemist, in 1817. The metal was first prepared pure by Bunsen and Matthiessen in 1855. Lithium is a comparatively rare metal, being found principally in the rare minerals *amblygonite*, *spodumene*, *petalite*, *lepidolite*, and *triphylite*; the water of many mineral springs contains it in considerable quantity, while traces of it have been detected by means of the spectroscope in sea-water, in many minerals and meteorites, as well as in various plants.

53. Preparation and Properties.—Metallic lithium is best obtained by the electrolysis of lithium chloride. On a large scale a mixture of potassium and lithium chlorides is electrolyzed. It is a brilliant, silver-white metal, somewhat softer than lead, and tarnishes in the air. It is remarkable as the lightest of the solid metals, having a specific gravity of only .534 at 20° C. It melts at 186° C., is ductile, and can be welded at ordinary temperatures, and burns in the air when more strongly heated. It bears a general resemblance to potassium and sodium, but it is harder and less easily oxidized than these metals. It decomposes water rapidly at ordinary temperatures, but does not burn on it. Its spectrum is characterized by an intense crimson line.

COMPOUNDS OF LITHIUM

54. Some of the principal compounds of lithium are *lithium chloride*, LiCl , a deliquescent, fusible, and volatile salt; the *oxide*, Li_2O , and the *hydroxide*, LiOH , the latter a caustic, strongly alkaline substance; the *carbonate*, Li_2CO_3 ; the *sulphate*, Li_2SO_4 ; and the *phosphate*, Li_3PO_4 , all of which are well-defined salts. (U. S. P., pages 257, 258, and 259.)

COPPER, GOLD, AND SILVER

COPPER

Symbol Cu. Atomic weight 63.57. Molecular weight 63.57. Valence I and II.

55. History and Occurrence.—Copper has been known from the earliest times. The Romans obtained it from the island of Cyprus and called it *aes Cyprium*, a term that afterwards became *cuprum*, from which the English word *copper* is derived. It is found abundantly in nature, both free and in combination. Native copper occurs in masses of great size near Lake Superior, while sulphide and carbonate ores are found in Canada, Montana, and Arizona. Large deposits of copper-bearing ore are also found in Australia, Chile, Peru, and in Russia and Siberia. The names of the principal copper ores and their chemical compositions are as follows: *Cuprite*, Cu_2O ; *cuprous sulphide*, CuS , in *copper glance*, and associated with sulphide of iron in *copper pyrites*; as *basic carbonate*, in *malachite*, $\text{Cu}_2(\text{OH})_2\text{CO}_3$; and in *azurite*, $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$. In addition to these minerals, from which copper is extracted on a large scale, mineral silicates, phosphates, arsenates, and oxychloride are known. Copper is also found in the coloring matter of the red wing feathers of certain birds.

56. Preparation.—The method applied for the extraction of copper varies with the ore under treatment. The oxides and carbonates are simply heated with charcoal or other fuel, with the addition of some silicious flux. The process of extracting copper from a mixture of copper sulphides and oxidized ore is a more complex operation.

57. Chemical Reactions.—Copper possesses a greater affinity for sulphur and a smaller affinity for oxygen than the metals (especially iron) with which it is associated.

The separation of the copper from the sulphide ores is not easy and requires careful and prolonged treatment. The various processes through which the copper ore must pass, before a sufficiently pure copper is obtained, may be classified as follows: (a) Heating and roasting; (b) calcination; and (c) poling.

58. Method of Extraction From Copper Ore.

During the *heating and roasting process* the ore is first moderately heated; part of the sulphur and arsenic is oxidized and passes off as sulphur dioxide and arsenic trioxide, respectively. This operation is regulated so that the sulphur retained is sufficient to combine with the whole of the copper to form cuprous sulphide, Cu_2S , the iron and part of the copper being transformed into oxide. The charge is then brought to a fusion at a higher temperature, when the ferrous oxide enters into combination with the silica, either originally contained in the ore or added to the charge to form a slag of ferrous silicate. By repetition of roastings and fusions the iron is thus ultimately removed.

59. In the *calcination process* the cuprous sulphide is, first, partly oxidized during a moderate temperature. Then, the temperature is raised so that the cuprous oxide formed may react with the sulphide:



The remainder of the sulphur is thus eliminated and metallic copper obtained. Any sulphide of iron that still remains is also acted on by the cuprous oxide as follows:



60. In the heating, roasting, or calcination of ores and materials used or manufactured by chemical plants, the *reverberatory furnace* is frequently used, and a brief description of this type of furnace is therefore important.

The material to be heated is placed on the bed, or hearth, *B* of the furnace, Fig. 3, and exposed to the direct action of the flame and gases, which pass from one end *F* of the furnace to the other and are deflected toward the hearth by the semi-

arched construction of the furnace roof. The charge is introduced at the hoppers *C* and spread over the bed of the furnace, being worked from the doors *D*, and finally withdrawn through openings in the bed of the furnace, not shown in the figure, and shot down into the vault *G*, while the volatile products escape through the flue. The course of the discharge exits is shown by dotted lines in the illustration.

61. In the *poling process*, the crude, or *blister*, copper obtained by any one of the numerous processes in use, is further refined by an operation known as *poling*. In this operation, the crude copper is melted in an oxidizing atmosphere on the hearth of a furnace. Coal is then sprinkled on the surface of the molten metal and the mass agitated with a



FIG. 3.

green log. In this manner any cuprous oxide is reduced by the action of the carbon in the coal and by the hydrocarbons* of the wood passing through the molten metal.

62. Other Processes.—Copper, 99.8 per cent. pure, is now obtained in this country by *electrolytic processes* in which a current of electricity is passed through a bath of copper sulphate, in which are suspended crude copper ingots or plates which act as anodes and pure sheets of copper which act as the cathodes. When the current is turned on, copper is dissolved from the anodes and is deposited on the cathodes, while the impurities are either dissolved or sink about the anodes to the bottom of the bath.

*Hydrocarbons. (See *Organic Chemistry for Pharmacy Students*.)

The copper in low-grade sulphide ores is now most profitably recovered by what is called the *flotation process*. The separation of copper in this process is dependent upon the fact that when the ore is finely ground and violently agitated in water containing an oil, preferably pine oil, by means of compressed air, a tough froth is formed which floats the metallic particles of copper but which allows the gangue, or ordinary rock, to sink to the bottom of the tank.

63. Properties.—Copper is a lustrous, sonorous metal of a peculiar red color and transmits a greenish blue light. Its specific gravity is 8.95, and it is somewhat softer than iron. When rubbed with the hand it exhales a peculiar, disagreeable odor. It conducts heat and electricity very readily. It may be drawn into fine wire or beaten into thin leaves, as its tenacity is considerable, being next to iron. Copper melts at 1,065° C. in air and may be volatilized by the heat of the oxyhydrogen blowpipe. It is unaltered in dry air at ordinary temperatures, but it absorbs oxygen in the presence of moisture and carbon dioxide. Green spots then appear on the surface, constituting a basic carbonate of copper, which is the compound commonly known as *verdigris*. At a high temperature it absorbs oxygen very eagerly, being converted into black cupric oxide, if the oxygen is in excess; or into red cuprous oxide, if the metal is in excess. The oxidation of copper is accelerated if the metal is in a state of fine division; in fact, when very finely powdered it often takes fire spontaneously. Weak acids, alkalies, and saline solutions act on it slowly in the presence of air; hence, as all its salts are more or less poisonous, anything to be taken as food should not be prepared in vessels made of copper or any of its alloys.

Copper is much employed for the construction of boilers, stills, etc. Owing to its high electric conductivity, enormous quantities of it are used in construction for cables, dynamos, etc. Sheet copper is used for coating the bottoms of ships, for roofing, etc.

SALTS OF COPPER

64. Classification.—Copper forms two series of salts. It acts as a bivalent element in the principal series, which contains such well-known compounds as CuCl_2 , CuSO_4 , CuS , and CuO ; these are generally spoken of as *copper compounds*, though to distinguish them from the other series they are frequently called *cupric compounds*. Another series of salts, of which some of the members are apparently represented by the formulas CuCl , Cu_2O , Cu_2S , etc., is also known; these are called *cuprous compounds*. In this series, copper appears to be univalent, though it has been suggested that in these compounds copper is also bivalent, and that the formulas should be written

$\text{Cu}-\text{Cl}$

Cu_2Cl_2 , etc., or $\begin{array}{c} | \\ \text{Cu}-\text{Cl} \end{array}$, etc. A determination of the vapor

density of cuprous chloride seemed to point to the double formula, Cu_2Cl_2 , but the results were not conclusive, and so long as nothing definite is known of the composition of these compounds, it seems reasonable to use the simplest formula.

65. Cuprous Oxide.—Cuprous oxide, Cu_2O , is found in nature, as *cuprite*, in either vitreous masses or red octahedral crystals. It is ordinarily prepared in the wet way by boiling a solution of copper acetate with glucose; a bright-red, crystalline powder is precipitated, which is anhydrous cuprous oxide. When heated in contact with air it absorbs oxygen and is converted into cupric oxide.

When potassium hydroxide is added to a solution of cuprous chloride, a yellow precipitate of cuprous hydroxide is thrown down. Cuprous oxide is used to impart a red color to glass.

66. Cupric Oxide.—Cupric oxide, CuO , occurs in nature as the mineral *melanconite*. It may be prepared by heating the metal in the air, or by calcining the hydrate, carbonate, or nitrate. It occurs in isometric forms—perhaps also in orthorhombic—but is generally massive. Its specific gravity is 6.3, and it fuses without change at a bright-red heat. Cupric oxide is easily reduced by both hydrogen and charcoal, with forma-

tion of either water or carbon dioxide, and hence is frequently used in organic analysis. It colors glass a beautiful emerald green. *Cupric hydrate*, $\text{Cu}(\text{OH})_2$, is thrown down as a pale-blue precipitate on adding sodium hydrate to a cold solution of a cupric salt. It is strongly basic and forms numerous salts.

67. Cupric Sulphide and Cuprous Sulphide.

Cupric sulphide, CuS , is found in nature as the mineral *covelite*. It is the black precipitate obtained when copper salts are precipitated by hydrogen sulphide. *Cuprous sulphide*, Cu_2S , also occurs in nature, forming the mineral *chalcocite*. It may be prepared by exposing finely divided copper or copper foil to sulphur vapor. It crystallizes in orthorhombic prisms, is blackish gray in color, has a metallic luster which is frequently tinged with green, and is easily fusible.

68. Cuprous Chloride.—Cuprous chloride, CuCl , is formed by burning copper in chlorine or by the action of reducing agents, such as sulphurous acid, zinc dust, or metallic copper, on cupric chloride. If, therefore, cupric oxide is dissolved in concentrated hydrochloric acid, the solution when boiled with excess of copper contains cuprous chloride, which is deposited as a white powder when it is poured into a large quantity of water. This, on exposure to air, turns green, owing to the formation of a basic chloride. The solution of cuprous chloride absorbs carbon monoxide and is used for determining the amount of this gas in certain gaseous mixtures; in presence of acetylene, C_2H_2 , a basic cuprous acetylide is formed, from which pure acetylene may be liberated by treatment with acid.

69. Cupric Chloride.—Cupric chloride, CuCl_2 , is formed when metallic copper or cuprous chloride is heated in excess of chlorine. It crystallizes in green needles with 2 molecules of water. It is obtained as a green solution by digesting cupric oxide with concentrated hydrochloric acid, and adding water.

70. Cupric Sulphate.—Cupric sulphate, CuSO_4 , more commonly known as *copper sulphate* or *blue vitriol*, can be prepared by treating almost any cupric compound, as the hydrox-

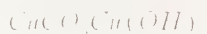
ide, carbonate, etc., with sulphuric acid. It is frequently prepared on a large scale by treating cupric sulphide with sulphuric acid. The simplest process consists in boiling copper turnings and clippings with sulphuric acid, sulphur dioxide being disengaged and the cupric sulphate formed. In the arts, the operation is conducted in lead-lined wooden tanks heated by steam.

Cupric sulphate crystallizes in large, blue, prismatic crystals that contain 5 molecules of water. When exposed to dry air, they effloresce superficially; heated to 100° they lose 4 molecules of water, disengaging the fifth only at 220° C. to 260° C. The anhydrous salt is white. At a high heat, cupric sulphate is decomposed into cupric oxide, sulphur dioxide, and oxygen. Cupric sulphate dissolves in 4 parts of cold and 2 parts of boiling water, and the concentrated solution has a pure blue color. It is insoluble in alcohol.

When an excess of ammonia is added to a solution of cupric sulphate a beautiful, dark-blue liquid is obtained. It contains ammoniacal cupric sulphate, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, which separates as dark-blue crystals when alcohol is added to the aqueous solution.

Cupric sulphate is employed as a caustic applicable to diseases of the eye. In the arts, it is used in the preparation of *blue ashes*, a mixture of calcium sulphate and cupric hydrate, made by decomposing cupric sulphate with milk of lime. It is much used in dyeing, particularly in dyeing black on wool and cotton; it is also employed for preserving wood. Large quantities of sulphate of copper are employed for electrotyping and electric batteries. (U. S. P., pages 128 and 620.)

71. Carbonates of Copper.—When cold solutions of sodium carbonate and cupric sulphate are mixed, a bluish-green precipitate is obtained, and at the same time carbon dioxide is disengaged. The precipitate becomes green when washed with warm water. It is known as *mineral green*, and can be regarded as a combination of 1 molecule of cupric carbonate with 1 molecule of cupric hydrate. It contains:



A similar compound exists in nature, constituting *malachite*. This mineral occurs in green masses. When cut and polished, it presents veins of various tints, and is fashioned into ornamental objects. Verdigris has the same composition.

Azurite, or *mountain blue*, which crystallizes in beautiful, blue, oblique rhombic prisms, can be regarded as a compound of 2 molecules of cupric carbonate with 1 of the hydrate:



SILVER

Symbol Ag. *Atomic weight* 107.88. *Molecular weight* 107.88. *Valence* I.

72. History and Occurrence.—Silver has been known in the metallic form from the earliest historic times. The ancient alchemists gave to it the name of Luna, from its bright white color.

It is found in a free state in the United States, Mexico, Peru, and many other countries. Its most important ores are *argentite*, Ag_2S ; *pyrargyrite*, Ag_2SbS ; and *horn silver*, AgCl . It is found also in combination with lead sulphide, copper sulphide, and many other ores.

73. Preparation.—The process employed for the extraction of silver varies, naturally, with the quality of the ore. At Freiberg, in Germany, the ore—an impure sulphide—is roasted with 10 per cent. of salt; the resulting mass is ground to a fine powder, and agitated in revolving barrels containing water and scrap iron, by which the silver is reduced to the metallic state. Mercury is then added to dissolve the silver, and by distilling the amalgam thus obtained the silver is left pure. In this country most of the silver is obtained in the lead-smelting process, or in connection with gold, by amalgamation, or one of the lixiviation processes.

The most common method employed in the United States consists of mixing the silver ore with other ores rich in lead and smelting this mixture with iron (either as scrap or as iron ore), limestone, and coke in a blast furnace. The silver-lead alloy

obtained (base bullion) usually contains gold, some copper, antimony, bismuth, etc. The base bullion is melted and then allowed to cool almost to the point of solidification, when the copper, bismuth, antimony, etc. rise to the top of the molten mass, and are skimmed off. The greater portion of the lead in the base bullion is then removed either by melting the mass and allowing it to cool slowly when pure lead crystallizes out, or by adding zinc to the molten mass and cooling. An alloy of lead-silver zinc, rich in silver, now rises to the surface and is skimmed off. The zinc is expelled by distillation and the lead removed by *cupellation*, which consists in injecting a blast of air into a *cupel* formed by depressing the bed of a reverberatory furnace. By this operation the lead is converted into the volatile litharge, PbO . Any gold obtained in the base bullion will be found with the silver after cupellation.

74. Properties.—Pure silver is a remarkably white, lustrous metal of specific gravity 10.5, and capable of taking a high polish. It is the best metallic conductor of heat and electricity known, is harder than gold, and is very ductile and malleable, although working of silver hardens it and it must be softened repeatedly by heating to a dull redness. It crystallizes in regular octahedra, melts at 961.5°C. , and may be distilled at the highest temperature of the oxyhydrogen blowpipe. When melted, silver is capable of absorbing twenty-two times its own volume of oxygen, which, however, is again evolved when it solidifies. It is unaltered in the air at any temperature, though it is readily acted on by chlorine, sulphur, and phosphorus. It is readily soluble in nitric acid, but difficultly soluble in hydrochloric and sulphuric acids. The alkalis have no action on it; for this reason silver vessels are used in the laboratory for fusing potassium hydrate and concentrating its solution. By the action of certain reducing agents on silver salts, the metal is obtained in a finely divided condition, in which form it shows brilliant golden, ruby, blue, and other colored tints.

75. Uses.—Owing to its softness, silver is rarely used in the pure state. It is generally alloyed with copper, which, while it greatly increases its hardness, scarcely alters its color.

The silver-coin alloy of the United States and France contains 10 per cent. of copper, that of England 7.5 per cent. The silver used in silver plate usually contains from 70 to 95 per cent. of pure silver.

By means of *electroplating* the surface of baser metals is provided with a coating of silver, by connecting them to the negative (or zinc) pole of the galvanic battery, and immersing them in a solution made by dissolving silver cyanide in potassium cyanide (a solution of potassium cyanide in 10 parts of water, with 3.5 grams of silver chloride dissolved in each pint of the liquid, will answer the purpose nicely), the positive (copper or platinum) pole being connected with a silver plate, also immersed in the solution. The electric current gradually decomposes the silver cyanide, and this metal is deposited on the object connected with the negative electrode, while the cyanogen liberated at the silver plate attacks the silver, so that the solution is always maintained at the same strength; the quantity of silver dissolved at this electrode is precisely equal to that deposited at the opposite one. (U. S. P., page 546.)

COMPOUNDS OF SILVER

76. Silver Oxide.—Silver oxide, Ag_2O , is usually prepared by adding a strong, hot solution of silver nitrate to one of potassium hydroxide. It is a dark-brown powder with a specific gravity of 7.2. It is readily decomposed by heat, and partly decomposed by light, into metallic silver and oxygen. It is only slightly soluble in water when freshly prepared; ammonia dissolves it readily, the solution depositing a violently explosive crystalline compound. *Silver hydroxide*, $AgOH$, is a strong base, is alkaline, and becomes silver oxide on heating to $60^\circ C$. (U. S. P., page 62.)

77. Silver Sulphide.—Silver sulphide, Ag_2S , occurs in nature as *silver glance*, or *argentite*, crystallized in regular octahedrons. It is soft, and can be scratched with the finger nail. It is prepared either by heating together silver and sulphur or by precipitating silver salts with hydrogen sulphide.

78. Silver Chloride.—Silver chloride, $AgCl$, occurs in nature as the mineral *cerargyrite*. It may be obtained by the direct union of silver and chlorine or by precipitating a solution of silver nitrate by a chloride. A white, curdy mass, soluble in ammonium hydrate, but insoluble in nitric acid, is thrown down, which, on drying, becomes a white powder. When heated to $451^{\circ} C.$, it fuses to a dark-yellow liquid, and on cooling solidifies to a translucent mass resembling horn, whence the name *horn silver*, sometimes applied to it. It has a specific gravity of 5.5, crystallizes in isometric forms, and turns black on exposure to light. For the latter reason it is used in photography.

If recently precipitated and moist silver chloride is placed on a sheet of zinc, in a short time a dark color will appear on the borders of the chloride, and the whole of that body will soon be converted into a dark-gray powder of finely divided silver, zinc chloride being at the same time formed. This reaction takes place much more rapidly if the silver chloride is moistened with hydrochloric acid, in which case the reduction is effected by nascent hydrogen produced by the action of the hydrochloric acid on the zinc.

79. Silver Bromide and Silver Iodide.—Silver bromide, $AgBr$, and silver iodide, AgI , are both found in nature in Mexico and Chile. Silver bromide may be obtained on adding hydrobromic acid, or a bromide of an alkali metal, to a solution of silver nitrate, as a yellowish-white, curdy precipitate, which is insoluble in nitric acid and nearly so in dilute ammonia—whereby it is distinguished from silver chloride—and melts at $426^{\circ} C.$, forming a reddish liquid. The precipitated bromide, when exposed to light, changes its color and assumes a grayish tint.

Silver iodide is a yellow, insoluble precipitate, produced by adding silver nitrate to potassium iodide. It is insoluble, or nearly so, in ammonia, and in this respect forms an exception to silver salts in general. It blackens on exposure to light, and melts at $555^{\circ} C.$ to a yellow liquid, which becomes brown on continued heating.

80. Silver Nitrate.—Silver nitrate, $AgNO_3$, or *lunar caustic*, is prepared by dissolving pure silver in nitric acid and allowing it to crystallize, or the solution is evaporated and the residue fused and cast into sticks. It crystallizes in rhombic tables or plates that melt at $218^\circ C.$, have a specific gravity of 4.3, and are readily soluble in alcohol and water. It is odorless, has a bitter, metallic taste, and a caustic action, rapidly blackening and destroying organic matter. It does not blacken in the air unless organic matter is present. Thus, it stains the fingers black when exposed to the light, but the stain may be removed by potassium cyanide, or, more safely, by tincture of iodine.

Silver nitrate is used in photography, in medicine, and to some extent in marking inks for linen and cotton goods, since the deposit of metallic silver formed on exposure to the light is not affected by washing. (U. S. P., pages 61, 62, 547, 571, and 572.)

81. Silver Nitrite.—Silver nitrite, $AgNO_2$, was first obtained by Proust. It is prepared by mixing warm solutions of silver nitrate and potassium nitrite. On cooling, silver nitrite separates in white crystalline needles slightly soluble in water, and decomposing, without fusion, when heated to $180^\circ C.$ It dissolves in boiling water with partial decomposition.

82. Silver Sulphate.—Silver sulphate, Ag_2SO_4 , is the final product obtained when silver sulphide is roasted in the air. It is also prepared by dissolving metallic silver in hot sulphuric acid. It crystallizes in small rhombic prisms that are isomorphous with anhydrous sodium sulphate. It is difficultly soluble in water, fuses at $660^\circ C.$, and decomposes at a high temperature. (U. S. P., page 547.)

83. Silver Sulphite.—Silver sulphite, Ag_2SO_3 , is precipitated as a white curdy mass when sulphurous acid is added to a solution of silver nitrate. It is insoluble in water, blackens in the light, and decomposes at $100^\circ C.$

84. Silver Orthophosphate.—Silver orthophosphate, Ag_3PO_4 , is formed as a yellow precipitate when a solution of

sodium orthophosphate is added to a solution of silver nitrate. It is soluble in nitric acid, but insoluble in water. It is affected by the light, turns brown on heating, and melts at 849° C. It is used in photography.

85. Silver Arsenite and Silver Arsenate.—Silver arsenite, Ag_3AsO_3 , is obtained as a yellow precipitate insoluble in water and alcohol when a mixture of the solutions of silver nitrate and arsenious acid is made just ammoniacal in the cold. If this solution is boiled, metallic silver separates. It is soluble in an excess of ammonium hydrate. Silver arsenate, Ag_3AsO_4 , is obtained as a reddish-brown precipitate when silver nitrate is added to arsenic acid. It is soluble in nitric acid and ammonium hydroxide.

GOLD

Symbol Au. Atomic weight 197.2. Molecular weight 197.2. Valence I and III.

86. Occurrence and Preparation.—Gold occurs widely distributed in nature, though in small quantities, as a rule. It is almost always found in the metallic state, usually associated, however, with certain quantities of silver, copper, or iron, and also in special ores, with bismuth and tellurium. Many minerals, such as galena, iron pyrites, and zinc blende, contain traces of gold. Though one of the rare metals, it is widely distributed; the chief localities where it is mined are the Rocky Mountains and Pacific Coast States in this country, Australia, South Africa, and the Klondike. It is found generally in quartz veins intersecting metamorphic rocks of various ages, and in the alluvial detritus (gravel) that has resulted from the disintegration of these rocks. To extract gold from auriferous quartz, the whole is first powdered roughly by mechanical means, and then subjected to separation in sluices, so arranged that the heavier particles containing the gold collect at the bottom of the sluice, while the gangue is carried off by the stream of water. The gold is separated by causing it to form an amalgam with mercury, or to collect on amalgamated copper

plates. The mercury is finally distilled off, leaving the gold behind as residue.

87. In the *chlorination process* the ore (iron pyrites or sulphide concentrates from stamp mills) is roasted, so that the iron is transformed into ferric oxide, which is not readily attacked by moist chlorine, and then subjected to the action of chlorine. The gold is thus converted into chloride, which can be dissolved out in water, and metallic gold precipitated from the solution by the addition of reducing agents, such as ferrous sulphate.

Potassium cyanide is now largely used for extracting gold, as it readily dissolves in this reagent.

The separation of silver and copper from gold may be effected by *quartation*, the success of which, as the name implies, depends on the gold being present to the extent of not more than one-quarter of the mass of metal employed. The metal is boiled with strong sulphuric acid, and the silver and copper are thus converted into sulphates, so that on lixiviation with water these are dissolved and the gold left as residue.

88. Properties.—Gold is a soft, orange-yellow metal of great brilliancy. Its physical character renders it very conspicuous among the metals; it is the heaviest of metals in common use, with the exception of platinum, its specific gravity being 19.32. In malleability and ductility it surpasses all other metals; the former property is turned to advantage for the manufacture of gold leaf, for which purpose a bar of gold, containing 96.25 per cent. of gold, 2.5 per cent. of silver, and 1.25 per cent. of copper, is passed between rollers that extend it into the form of a broad ribbon; this is cut into squares that are packed between layers of fine vellum, and beaten with a heavy hammer; these thinner squares are then again cut up and beaten between layers of gold-beater's skin until they are sufficiently thin. An ounce of gold may thus be spread over 100 square feet; 282,000 of such leaves placed on one another form a pile only 1 inch high. The gold leaves transmit green light, though when rendered non-lustrous by heat this light is ruby red.

Although fusing about the melting point of copper, gold is seldom cast, on account of its great contraction during solidification. Gold crystallizes in isometric forms, conducts heat and electricity well, and fuses at $1,061.7^{\circ}\text{C}$. It is unaltered in the air, and is not attacked by any single acid or alkaline hydroxide, though solutions that contain free chlorine, like aqua regia, dissolve it readily.

Gold is used both for jewelry and coinage. Being too soft, alone, for either purpose, it is alloyed with copper or silver, the mint alloy of the United States consisting of 9 parts of gold and 1 of copper. The purity of gold for jewelry is estimated by the *carat*, pure gold being 24 carats fine; hence, an alloy of 18 parts of gold to 6 of silver and copper is said to be 18 carats fine.

COMPOUNDS OF GOLD

89. Oxides of Gold.—Three compounds of gold and oxygen are known, namely: Au_2O , Au_3O_2 , and an auro-auric oxide, $(\text{AuO})_4$.

Aurous oxide, Au_2O , is a violet-colored powder obtained when aurous chloride is treated with potassium hydroxide. Hydrochloric acid forms metallic gold and the trichloride, thus:



Heated to 250°C . it decomposes into gold and oxygen. Sulphuric acid and nitric acid do not affect it.

Auric oxide, Au_2O_3 , is obtained as a brown powder by gently heating auric hydroxide, obtained by treating a hot solution of auric chloride with a hot solution of sodium hydroxide. Heat decomposes this oxide into metallic gold and oxygen. It is soluble in nitric acid. Potassium hydroxide dissolves it, forming *potassium aurate*, KAuO_2 .

90. Chlorides of Gold.—*Auric chloride*, AuCl_3 , is formed when gold is dissolved in aqua regia, and if this solution is evaporated, the auric chloride is partly decomposed, with the formation of *aurous chloride*, AuCl . It is formed also by passing chlorine gas through water containing finely divided gold in solution. It melts at 288°C ., when heated in a sealed

tube. Auric chloride may be obtained in crystals containing 2 molecules of water of crystallization, $AuCl_3 \cdot 2H_2O$. When a solution of auric chloride is treated with stannous chloride, a purple precipitate, known as *purple of Cassius*, is formed. This appears to be metallic gold in a finely divided condition. When dry auric chloride is gently heated, it is decomposed into chlorine and aurous chloride, and if this is treated with water it is decomposed into auric chloride and gold. (U. S. P., pages 69, 70, and 534.)

91. Sulphides of Gold.—*Auric sulphide*, Au_2S_3 , is precipitated from a cold solution of a gold salt by hydrogen sulphide, as a black or brownish-black mass, which is accompanied by free sulphur. This sulphide is very unstable, and forms soluble compounds when treated with alkaline sulphides.

Aurous sulphide, Au_2S , is precipitated as a steel-gray substance when a hot solution of a gold salt is treated with hydrogen sulphide. This sulphide dissolves in pure water, and is reprecipitated from this solution by hydrochloric acid.

CALCIUM, STRONTIUM, AND BARIUM

CALCIUM

Symbol Ca. *Atomic weight* 40.07. *Molecular weight* 40.07. *Valence* II.

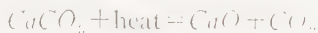
92. History and Occurrence.—Calcium carbonate and calcium sulphate were known to the ancients, the former being burned into lime for making mortar. It is from the Latin word for lime, *calx*, that the name calcium has been derived. The metal itself was discovered by Davy in 1808 and isolated in 1855 by Matthiessen, who obtained it by decomposing fused calcium chloride by means of the voltaic current. It is found abundantly in the mineral kingdom. As carbonate it forms the mineral calcite and the rock masses known as *limestone*, *chalk*, and *marble*. As sulphate, it forms vast beds of *gypsum*; as phosphate, it occurs as *apatite*; as fluoride, in *fluorspar*, etc. It also occurs as the phosphate in the bones of

animals, in the shells of eggs and oysters, and in nearly all spring and river waters.

93. Preparation and Properties.—Metallic calcium may be obtained by the electrolysis of the fused chloride, or by heating an alloy of zinc and calcium to a high temperature to distil off the zinc and leave the calcium. The alloy is prepared by fusing together a mixture of calcium chloride, zinc, and sodium, when the sodium decomposes the chloride, and the calcium and zinc form an alloy; also, by the reduction of the oxide by heating with magnesium. Metallic calcium has a light-yellow, brilliant color, is about as hard as gold, and is very ductile and malleable. It oxidizes slowly in the air, though it is permanent in perfectly dry air. It decomposes water at ordinary temperatures. Its specific gravity is 1.57. The salts of calcium impart a brick-red tinge to an otherwise colorless flame.

COMPOUNDS OF CALCIUM

94. Calcium Oxide.—Calcium oxide, CaO , commonly known as *lime* or *quicklime*, is always prepared on a large scale by igniting its carbonate. Thus,



Pure calcium oxide is a white amorphous powder which may be fused in the electric furnace at a temperature of about $2,570^\circ \text{C}$. It is only slightly soluble in water, but the dry material quickly absorbs water from the air, calcium hydroxide being formed. (U. S. P., pages 95 and 96.)

95. Calcium Hydroxide.—Calcium hydroxide, Ca(OH)_2 , generally known as *slaked lime*, is usually formed by adding water to the oxide; thus,



It is a soft, white, bulky powder, and is slightly soluble in water, forming an alkaline; feebly caustic liquid known as *lime water*. Lime water readily absorbs CO_2 from the atmosphere, becoming milky, and precipitates CaCO_3 . Calcium hydroxide is easily converted into calcium oxide by heat. It

is widely used in manufacturing chemistry, being the cheapest alkaline substance. (U. S. P., pages 239 and 528.)

96. Calcium Chloride.—Calcium chloride, CaCl_2 , is produced by dissolving either calcium oxide or carbonate (chalk or white marble, for instance) in hydrochloric acid, and is frequently obtained as a waste product in the chemical arts, as in the manufacture of ammonia from ammonium chloride and quicklime:



On evaporating a solution of calcium chloride in water, prismatic crystals of the composition $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ are obtained. These crystals, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, lose 2 molecules of water when dried in vacuo, and the whole 6 molecules when heated above 200°C . The calcium chloride thus obtained, free from water, is used as a drying agent in the laboratory, as it possesses a great eagerness to combine again with water. In consequence of the attraction of calcium chloride for water, surfaces wetted with a solution never get dry, and this solution is, consequently, frequently employed to make mantelets, for the protection of gunners, and also to render various objects, such as ropes, scenery, etc. in theaters, reasonably fireproof.

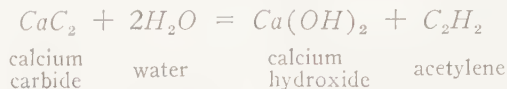
The crystals of calcium chloride are used with snow as a freezing mixture; in it a thermometer falls to -48.5°C . Calcium chloride melts at 774°C ., and if heated in the air evolves chlorine. A saturated solution of calcium chloride boils at 180°C ., and is sometimes used in the laboratory as a convenient bath for obtaining a temperature above the boiling point of water. (U. S. P., pages 89, 90, and 91.)

97. Calcium Carbide.—Calcium carbide, CaC_2 , is now prepared on a large scale by intensely heating a mixture of lime and carbon in the electric furnace, the following reaction taking place:



Calcium carbide is usually a dark-gray or bronze-colored, homogeneous, crystalline mass having a specific gravity of 2.2. When heated in the air it burns into calcium carbonate, CaCO_3 .

Water instantly reacts with it, forming calcium hydroxide and acetylene, according to the equation:



98. Calcium Nitrate.—Calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, is formed in nature in the vicinity of dwellings, in the soils of cellars, in damp walls, and as an efflorescence on the walls of stables and other places through which urine or other organic liquids percolate; it is, consequently, frequently called *lime saltpeter*, or *wall saltpeter*. Calcium nitrate is deliquescent and soluble in water and alcohol.

99. Calcium Carbonate.—Calcium carbonate, CaCO_3 , occurs widely distributed in nature as the different varieties of limestone, marble, calcspar, and chalk. It is dimorphous, crystallizing in rhombic crystals having a specific gravity of 3, as *aragonite*, and in hexagonal rhombohedra with a specific gravity of 2.7, as *calcite*.

Limestone and *chalk* are either amorphous or indistinctly crystalline calcium carbonate, while *marble* is a granular crystalline form. Oxides of iron and manganese are sometimes present in marble and give it a variegated appearance. When bituminous matter is present it is known as black marble.

Calcium carbonate is nearly insoluble in pure water. The presence of carbon dioxide in water increases its solubility. Heated at 825°C ., calcium carbonate decomposes into quicklime and carbon dioxide. (U. S. P., pages 90 and 127.)

100. Calcium Sulphate.—Calcium sulphate, CaSO_4 , occurs in nature in combination with 2 molecules of water as *gypsum*, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. It is also found in nature in the anhydrous condition as the mineral *anhydrite*. In combination with water this compound also forms transparent prisms known as *selenite*. By heating gypsum to between 150° and 200°C . it loses water and forms *plaster of Paris*. This mixed with water combines with it and solidifies. When the gypsum is burnt it loses water and forms the hemihydrate, $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$. This is more soluble than either the anhydrous salt or the salt

containing 2 molecules of water, and part dissolves in the water and forms a saturated solution. The hydrate is thus formed and, as the solution is supersaturated with respect to the hydrate, some of it crystallizes out in this form, and the water thus released dissolves more of the hemihydrate. The process is thus repeated until the whole of the hemihydrate is converted into the hydrate. Plaster of Paris mixed with glue is frequently used for ornamental purposes under the name of *stucco*.

Precipitated calcium sulphate is used in the manufacture of paper, under the name of *pearl hardener*. Calcium sulphate is used in stables and farmyards for absorbing the ammonia of the decomposing animal excrements, which would otherwise be lost to the manure. It is contained in many natural waters, and is one of the chief causes of the permanent hardness that is not removed by boiling. It is sparingly soluble in water, so that the sulphates will precipitate calcium only from relatively strong solutions. The aqueous solution of CaSO_4 precipitates barium salts immediately, but strontium salts only after an interval, on account of the greater solubility of SrSO_4 . Calcium sulphate is most soluble in water having a temperature of 35°C .; 1 part of it then dissolves in 400 parts of water. It is insoluble in alcohol. Boiling HCl dissolves it, and deposits it in needle-shaped crystals on cooling. It is used also as a filler for writing papers.

101. Calcium Fluoride.—Calcium fluoride, CaF_2 , is found in nature as the mineral *fluorspar*. It occurs in small quantities in the bones and the enamel of the teeth, in the ashes of some plants, and in sea-water. It is insoluble in water and is only decomposed by strong acids. When heated it becomes luminous, fuses at a red heat, hence serves as a flux in the smelting of ores.

102. Calcium Sulphide.—Calcium sulphide, CaS , is obtained by heating calcium sulphate at a high temperature with charcoal. It is a yellowish-white mass that is luminous in the dark after having been exposed to the sunlight. This fact was first observed, by Marggraf in 1750. Canton in 1768

described a method for obtaining the sulphide by strongly heating oyster shells with sulphur.

Calcium hydrosulphide, $Ca(SH)_2$, is obtained when a cream of calcium hydroxide is acted on by hydrogen sulphide. It crystallizes in colorless prisms with 6 molecules of water and readily melts in its water of crystallization. Warmed in a stream of hydrogen sulphide it decomposes into calcium sulphide and hydrogen sulphide.

Calcium sulphide forms the main constituent in the tank waste of the alkali works. A solution of calcium hydrosulphide is used in tanneries as a depilatory. (U. S. P., page 94.)

103. Calcium Phosphate.—Calcium phosphate, $Ca_3(PO_4)_2$, occurs in combination with calcium fluoride in the minerals *apatite* and *phosphorite*. It forms approximately 80 per cent. of the ashes of all bones. Calcium phosphate is precipitated as a white gelatinous mass when disodium phosphate is added to an ammoniacal solution of calcium chloride. It is nearly insoluble in water but is soluble in hydrochloric acid, in nitric acid, and in acetic acid.

104. Primary Calcium Phosphate.—Primary calcium phosphate, $Ca(H_2PO_4)_2$, frequently called *acid calcium phosphate*, is prepared by the action of sulphuric acid on the normal phosphate. It is the chief constituent of the superphosphates used as fertilizers. It is prepared in the pure state by dissolving calcium phosphate in the required amount of phosphoric acid, and allowing the solution to evaporate when the salt crystallizes out in rhomboidal plates containing 1 molecule of water. It is readily soluble in water, and when heated changes to the metaphosphate, $Ca(PO_3)_2$.

105. Calcium Pyrophosphate.—Calcium pyrophosphate, $Ca_2P_2O_7$, is formed when *secondary calcium phosphate*, $CaHPO_4$, precipitated when disodium phosphate is added to a weak acetic-acid solution of calcium chloride, is strongly ignited. The pyrophosphate, when heated to a red heat, forms a perfectly transparent glass possessing all the properties of ordinary glass.

106. Calcium Silicates.—Calcium silicates are found, associated with silicates of other metals, in many minerals. They also enter into the composition of most glasses. Window glass, for instance, contains the silicates of calcium and sodium, and Bohemian glass those of calcium and potassium.

STRONTIUM

Symbol Sr. Atomic weight 87.63. Molecular weight 87.63. Valence II.

107. History and Occurrence.—Strontium was distinguished as a peculiar substance by Hope in 1792. Davy, in 1808, recognized it as an elementary body, though it was not until 1855 that Bunsen and Matthiessen obtained it in the pure state. Strontium occurs in nature both as sulphate and as carbonate. The former, known as the mineral *celestite* (so called from the blue tint of many specimens), is mostly found in beautiful crystals associated with the native sulphur in Sicily; the latter is found in the mineral *strontianite*—derived from Strontian, Scotland, where it was first found, and from which the metal obtained its name *strontium*.

108. Preparation and Properties.—Metallic strontium is usually prepared by the electrolysis of its chloride, though it has been obtained by distilling strontium amalgam in hydrogen. The amalgam was prepared by the action of sodium amalgam on a saturated solution of strontium chloride.

Strontium is a pale-yellow metal of specific gravity 2.54; it is harder than lead, is malleable and ductile, and melts at 900° C. If heated in air, it burns vividly with a characteristic crimson flame. Though it is quite permanent in dry air, it decomposes water readily, with the evolution of hydrogen.

COMPOUNDS OF STRONTIUM

109. Strontium Oxide.—Strontium oxide, or *strontia*, SrO , is, as a rule, obtained by igniting strontium nitrate, $Sr(NO_3)_2$. It is a grayish-white porous mass, is infusible, and unites energetically with water to form the hydroxide.

110. Strontium Dioxide.—Strontium dioxide, or peroxide, SrO_2 , crystallizes in pearly plates containing 8 molecules of water when a solution of the oxide or hydroxide in water is treated with hydrogen peroxide. On being heated the anhydrous dioxide remains as a light white powder, which gradually loses oxygen.

111. Strontium Hydroxide.—Strontium hydroxide, $Sr(OH)_2$, is obtained as the result of the union of strontium oxide and water. It is prepared on a large scale by heating celestite with brown iron ore and coal dust. It forms colorless, deliquescent, quadratic crystals having the formula $Sr(OH)_2 \cdot 8H_2O$. It is more soluble in water than is calcium hydroxide, is used in sugar refining, and when strongly heated is converted into strontium oxide.

112. Strontium Nitrate.—Strontium nitrate, $Sr(NO_3)_2$, is prepared in considerable quantity by dissolving strontium carbonate—usually the mineral strontianite—in nitric acid. It is largely used in pyrotechnics to produce red fire. It is soluble in water, but insoluble in alcohol.

113. Strontium Chloride.—Strontium chloride, $SrCl_2$, crystallizes in needles having the composition $SrCl_2 \cdot 6H_2O$, and having a bitter taste. It is deliquescent and fairly soluble in alcohol; the alcoholic solution burns with a red flame.

114. Strontium Bromide.—Strontium bromide appears as transparent, colorless, hexagonal crystals; odorless, but with a bitter taste. It is deliquescent in moist air. The salt may be obtained by neutralizing dilute hydrobromic acid with strontium carbonate, evaporating and crystallizing. (U. S. P., page 412.)

115. Strontium Iodide.—Strontium iodide appears as transparent, colorless plates; in crystalline crusts, or in a white, granular powder; odorless and with a bitter, saline taste. It is deliquescent and becomes yellow, when exposed to air and light. The salt may be made by evaporating a solution of hydriodic acid saturated with strontium hydroxide or carbonate. (U. S. P., pages 412 and 413.)

116. Strontium Carbonate and Sulphate.—The carbonate of strontium, *strontianite*, SrCO_3 , and strontium sulphate, *celestite*, SrSO_4 , are found in nature, as has been mentioned. They are insoluble in water, and are deposited as white precipitates on adding a soluble carbonate or sulphate to the solution of a strontium salt. Strontium sulphate is, however, less soluble than calcium sulphate and more soluble than barium sulphate. Strontium salts impart a red tinge to the flame of any substances with which they are in combination.

BARIUM

Symbol Ba. Atomic weight 137.37. Molecular weight 137.37. Valence II.

117. History and Occurrence.—Barium was first recognized as a new element by Scheele in 1774. Davy, in 1808, succeeded in isolating the metal. Its name is derived from the Greek word *barys*, meaning *heavy*, because of the high specific gravity of all the barium compounds. It occurs in nature largely as the sulphate in *heavy spar*, or *barite*; as *witherite*, or barium carbonate, and in lead and silver ores.

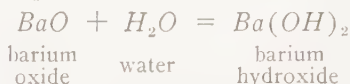
118. Preparation and Properties.—Metallic barium is prepared by the electrolysis of the fused chloride, or by the electrolysis of the carbonate or sulphate mixed with mercury and mercuric oxide and distilling the amalgam.

Barium is a silver-white malleable metal with a specific gravity of 3.7, melts at 850°C ., and boils at 950°C . It is stable in dry air but oxidizes rapidly in moist air, and decomposes both water and alcohol.

COMPOUNDS OF BARIUM

119. Barium Oxide.—Barium oxide, or *baryta*, BaO , is obtained by heating the nitrate. It is a heavy, gray, porous solid of specific gravity 5.5; it unites energetically with water, the action being accompanied by a hissing sound and the evolution of much steam. The product of the reaction, known as

caustic baryta, is the hydroxide $Ba(OH)_2$, which is obtained according to the equation:



Barium hydroxide is soluble in 2 parts of boiling water, and on cooling is deposited in large tabular crystals. The solution of barium hydroxide in water is known as *baryta water*. Crystallized barium hydroxide may be produced by adding 113 grammes of powdered barium nitrate to 340 cubic centimeters of a boiling solution of $NaOH$ containing 85 grammes of commercial caustic soda in 567 cubic centimeters of water; the solution becomes turbid from the separation of barium carbonate produced from the sodium carbonate in the hydroxide; it is boiled for some minutes and then filtered; on partial cooling, some crystals of undecomposed barium nitrate are deposited; and, if the clear liquid is poured off into another vessel and stirred, it deposits an abundant mass of crystals of barium hydroxide, having the composition $Ba(OH)_2 \cdot 8H_2O$. These crystals soon effloresce and become opaque when exposed to the air.

120. Barium Dioxide.—Barium dioxide, or peroxide, BaO_2 , is obtained by passing dry oxygen over barium oxide heated to dull redness. It is a gray, sometimes greenish-looking, porous substance, and loses its second atom of oxygen when heated to bright redness.

121. Barium Sulphide.—Barium sulphide, BaS , is obtained by reducing barium sulphate with charcoal, according to the equation:



or by passing hydrogen sulphide over heated barium oxide until no more water is formed.

Like calcium sulphide, it is phosphorescent. When dissolved in water, it is decomposed into barium hydroxide and barium hydrosulphide.

122. Barium Chloride.—Barium chloride, $BaCl_2 \cdot 2H_2O$, is the barium compound most used in the laboratory;

it may be obtained by saturating the solution of barium carbonate with hydrochloric acid. Barium chloride is deposited in tabular crystals, belonging to the type of the orthorhombic prisms, which are unaltered in the air and have the formula $BaCl_2 \cdot 2H_2O$. It is easily soluble in water, but insoluble in alcohol, as well as in strong acids. It is poisonous. (U. S. P., page 526.)

123. Barium Chlorate.—Barium chlorate, $Ba(ClO_3)_2$, is of importance because of its employment in pyrotechnics. It is prepared by adding barium chloride to a solution of sodium chlorate. On concentration the sodium chloride crystallizes out first and is separated from the solution, which is then evaporated and the chlorate purified by recrystallization. It crystallizes in shining, tabular prisms, with 1 molecule of water; it is readily soluble in water and alcohol. Mixed with sulphur and charcoal, it imparts a brilliant green color to the flame of the burning mixture.

124. Barium Nitrate.—Barium nitrate, $Ba(NO_3)_2$, is prepared by decomposing barium carbonate with dilute nitric acid, filtering and evaporating the solution. It crystallizes in regular octahedrons, the crystals being transparent and unaltered in the air. One part of barium nitrate requires for its solution about 20 parts of water at $12^\circ C$., 5 parts of water at $15^\circ C$., and 2.8 parts at $106^\circ C$. When heated to redness, barium nitrate gives off oxygen, nitrogen, and nitrogen dioxide, and is converted into barium oxide; thus,



Barium nitrate is used in the manufacture of pyrotechnics and explosives.

125. Barium Carbonate.—Barium carbonate, $BaCO_3$, occurs abundantly in nature as the mineral *witherite*, in shining rhombic prisms. It is prepared as a dense white powder with a specific gravity of 4.3, by pouring a solution of barium chloride into an excess of a boiling solution of sodium carbonate. It is insoluble in water, and fuses at a white heat, losing carbon dioxide and forming the basic carbonate $BaO \cdot BaCO_3$.

126. Barium Sulphate.—Barium sulphate, $BaSO_4$, found abundantly in nature as barite, or heavy spar, has a specific gravity of 4.5. It is almost insoluble in water and acids, except in concentrated sulphuric acid, when the solution, on cooling, deposits crystals of acid barium sulphate, $BaH_2(SO_4)_2$. *Artificial barium sulphate* is used by painters instead of white lead, under the name of *permanent white* (*blanc fixe*), and as an adulterant of white lead. It is also employed for glazing paper, cards, etc., and is prepared by mixing the solution of a barium compound with dilute sulphuric acid, when the barium sulphate separates as a white precipitate, which is collected, washed, and dried. The prepared barium sulphate has more body, or covering power, than the finely ground mineral.

MAGNESIUM, ZINC, CADMIUM, AND MERCURY

MAGNESIUM

Symbol Mg. *Atomic weight* 24.32. *Molecular weight* 24.32. *Valence* II.

127. History and Occurrence.—Magnesium carbonate, under the name of *magnesia alba*, has been known in Europe since the beginning of the 18th century, but, although Black in 1775 showed that this substance appeared to be a peculiar earth, its composition was not known until 1808, when Davy obtained the metal. The magnesium he obtained was rather impure; and not until 1830, and then by Bussy, was it produced in an approximately pure form. Bunsen and Matthiessen, in 1852, prepared it by electrolysis of fused magnesium chloride; and, in 1857, Deville and Caron obtained it in large quantities by acting on the chloride with sodium, a process subsequently improved by Sonstadt.

Magnesium is found abundantly, like calcium, in all three natural kingdoms, as *magnesite*, $MgCO_3$; *dolomite*, $CaMg$

$(CO_3)_2$; *Epsom salts*, $MgSO_4 \cdot 7H_2O$, etc. Among minerals containing this metal, those most frequently met with are certain combinations of silica and magnesia, well known by the names of *talc*, *steatite*, or *French chalk*, *asbestos*, and *meerschauum*; nearly all minerals containing magnesium possess a peculiar soapy feeling.

128. Preparation and Properties.—Magnesium may be prepared by the electrolysis of the chloride, but is more conveniently prepared by decomposing the chloride with sodium. In carrying out this process, magnesium chloride, fluorspar, and sodium are mixed and highly heated. As dry magnesium chloride is rather difficult to obtain, the double chloride of magnesium and potassium, $KMgCl_3$, is frequently substituted.

At the present time magnesium is prepared by the electrolysis of fused carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$. The carnallite is fused by external heat in a cylindrical steel vessel, which is made the cathode terminal. The anode is a carbon rod placed in a porcelain cylinder through which a current of coal gas or hydrogen is passed to remove all the oxygen and chlorine evolved. The metal magnesium separates at the cathode and floats on the surface of the fused electrolyte.

Magnesium is a silver-white, brilliant metal having a specific gravity of 1.76. It is somewhat malleable and ductile, but is not very tenacious. It melts at $650^\circ C.$, boils at $1,120^\circ C.$; and may be obtained crystallized in regular octahedrons. It oxidizes readily in moist air, but is not attacked by dry air. Acids attack it with ease, and it unites directly with most negative elements, including nitrogen. It burns when heated with an intense white light. It decomposes many salts with an evolution of hydrogen.

The light produced by burning magnesium is particularly rich in chemically active rays, producing chemical changes similar to those caused by sunlight, so that photographs may be made by its means in the absence of sunlight.

COMPOUNDS OF MAGNESIUM

129. Magnesium Oxide.—Magnesium oxide, or **magnesia**, MgO , occurs in nature as the mineral *periclasite* crystallized in isometric forms; it is the sole product of the combustion of magnesium in the air, and is left whenever the carbonate, hydroxide, or nitrate of magnesium is ignited. It forms a soft, bulky, white powder that slowly attracts moisture from the air, to form the hydroxide, $Mg(OH)_2$. Magnesia is employed in medicine and in the manufacture of refractory lining for furnaces. (U. S. P., pages 142, 168, 263, and 264.)

130. Magnesium Hydroxide.—Magnesium hydroxide, $Mg(OH)_2$, is found in nature as the mineral *brucite*. It is obtained as a white, gelatinous mass when potassium or sodium hydroxide is added to a solution of a magnesium salt. It can be dried at 100° C. without decomposition, but is decomposed into the oxide at a low red heat. It absorbs carbon dioxide from the air, and is almost insoluble in water. It is used to a great extent in extracting sugar from sugar beets.

131. Magnesium Chloride.—Magnesium chloride, $MgCl_2$, is most readily prepared by igniting the double chloride of magnesium and ammonium; the ammonium chloride is thereby driven off and the magnesium chloride left as a white, translucent, crystalline mass, readily fusible and somewhat volatile. It is very soluble in water, and deliquesces readily. It may be prepared also by the action of hydrochloric acid on magnesium carbonate or oxide. It occurs in spring waters, sea-water, and in various salt beds. It has a saline, bitter taste. (U. S. P., page 537.)

132. Magnesium Carbonate.—Magnesium carbonate, $MgCO_3$, occurs in nature in rhombohedra, isomorphous with calcite, as the mineral *magnesite*. It also occurs combined with calcium carbonate as *dolomite*. It is present in nearly all natural waters, causing temporary hardness, the magnesium carbonate being precipitated by boiling. It is obtained as a white voluminous powder by drying the precipitate formed when an alkali carbonate is added to a solution of a magnesium

salt. It has a bitter taste and an alkaline reaction. Magnesium carbonate is soluble in water containing carbon dioxide, but on boiling, it separates out in crystals containing 3 molecules of water. (U. S. P., pages 142, 262, and 263.)

133. Magnesium Sulphate. - Magnesium sulphate, $MgSO_4$, exists in solution in sea-water, and in certain purgative mineral waters, such as those of Epsom, in England, whence the name *Epsom salt*, so frequently applied to this substance. It also occurs as *kieserite*, $MgSO_4 \cdot H_2O$. It was formerly produced by heating dolomite and then treating the residue with sulphuric acid. It is now prepared by treating the crude kieserite on sieves with water, which dissolves the magnesium and sodium chlorides. The kieserite, together with insoluble impurities, drops through the sieves and is allowed to harden in conical wooden casks and is then dried and powdered. In this state it contains from 80 to 90 per cent. of magnesium sulphate. It is then purified by crystallization.

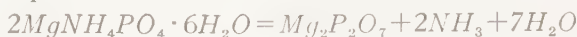
Magnesium sulphate crystallizes in small, colorless prisms or needles, with 7 molecules of water, has a bitter, saline taste, and is soluble in water. The crystals fuse easily and lose 6 molecules of water at $150^\circ C.$; the last molecule of water can, however, be driven off only at a temperature of $200^\circ C.$ or higher. From its intimate relationship to the compound, this last molecule of water is termed *water of constitution*.

Magnesium sulphate forms a series of double salts with the sulphates of the alkalies, of which the double sulphate of magnesium and potassium, $MgK_2(SO_4)_2 \cdot 6H_2O$, is an example. (U. S. P., pages 265 and 537.)

134. Phosphates of Magnesium.—The *normal orthophosphate*, $Mg_3(PO_4)_2$, is contained in the bones of animals and in the seeds of cereals. It is obtained as a hydrated white precipitate having the formula, $MgHPO_4 \cdot 7H_2O$, when disodium phosphate is added to the solution of magnesium salts.

Magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, is a frequent constituent of urinary calculi, and is precipitated by disodium phosphate from ammoniacal solutions of magnesium salts. The precipitation is greatly accelerated by stirring. It

is sparingly soluble in water, and nearly insoluble in ammonia. When heated it loses water and ammonia, forming magnesium pyrophosphate, thus:



ZINC

Symbol Zn. Atomic weight 65.37. Molecular weight 65.37. Valence II.

135. History and Occurrence.—Zinc occupies a high position among useful metals, being peculiarly fitted, because of its lightness and durability, for the construction of pipes, roofs, etc. An ore of zinc was used by the ancient Greeks, under the name *cadmia*, in the manufacture of brass. In Europe, zinc was first discovered in the 18th century, it having been, until that time, imported from China. The name *zinc* was given to the metal by Paracelsus in the 16th century.

The ores of zinc are found very abundantly in this country, in England, Transylvania, Hungary, and Silesia.

Metallic zinc, as a rule, does not occur free in nature, though it is claimed to have been found in the native state near Melbourne, Australia. The chief ores of zinc are the carbonates *zinc spar* and *calamine*, $ZnCO_3$; the sulphide, *zinc blende*, ZnS ; the oxide, *zincite*, or *red zinc ore*, ZnO ; the silicate, *willemite*, $2ZnO \cdot SiO_2$; *franklinite*, $(ZnFe)O \cdot Fe_2O_3$; *zinc spinel*, or *gahnite*, $ZnO \cdot Al_2O_3$.

136. Preparation.—Zinc is extracted from its ores by first roasting them in a reverberatory furnace and then distilling them, mixed with charcoal or powdered anthracite coal, in closed iron or earthen vessels. By the action of the carbon of the charcoal or coal, the oxygen is removed from the zinc oxide that constitutes the roasted ore, and the zinc thus set free, being volatile, distils over into suitable receivers.

137. Properties.—Zinc is a bluish-white, highly crystalline metal; its specific gravity is about 7; its fracture is laminated and brilliant. It is hard and brittle at ordinary tem-

peratures, and also at 200° C., but between 100° C. and 150° C. it is malleable and ductile and may be rolled into thin sheets. At 419° C. it melts, and at 918° C. it boils. When heated to redness in air, it volatilizes and burns with a greenish flame into a smoke of oxide that falls in bulky, white flakes, which were formerly known as *flowers of zinc*, or *philosopher's wool*.

Zinc dissolves with the evolution of hydrogen in hydrochloric and sulphuric acid, and in solutions of potassium and sodium hydroxides. When perfectly pure, it is dissolved with difficulty by dilute sulphuric acid at ordinary temperatures, and the easy solubility of the commercial metal must be attributed to the presence of small quantities of foreign metals.

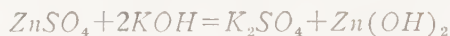
The great strength of iron has been ingeniously combined with the resistance of zinc to oxidation in the so-called *galvanized iron*. This is manufactured by coating clean iron sheets with melted zinc, thus affording a protection much needed in and around large towns, where the oxides of sulphur arising from the combustion of coal, and the acid emanations from various factories, greatly accelerate the corrosion of unprotected iron. The iron plates thus coated are at first thoroughly cleaned and then dipped into a vessel of melted zinc, the surface of which is coated with sal ammoniac (ammonium chloride), in order to dissolve the zinc oxide that forms on the surface of the metal and that might adhere to the iron plate, thus preventing its becoming uniformly coated with the zinc. A more firmly adhering coat of zinc is obtained by first depositing a thin film of tin on the surface of the iron plate by galvanic action, whence the name *galvanized iron* is derived. (U. S. P., pages 495, 496, and 553.)

COMPOUNDS OF ZINC

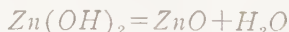
138. Zinc Oxide.—Zinc oxide, ZnO , occurs in nature as *red zinc ore*, or *zincite*. It is the sole product of the combustion of zinc in the air, and is also prepared by heating the carbonate or nitrate. It is used under the name of *zinc white* as a stable white paint, and is also used in medicine. It is prepared for medicinal purposes by igniting the basic carbonate

which is precipitated by treating a solution of zinc sulphate with sodium carbonate. It is an amorphous white powder, becoming a lemon yellow when hot, has a specific gravity of 5.78, absorbs carbon dioxide from the air, is insoluble in water but soluble in dilute acids, ammonium hydroxide, and ammonium carbonate. Heated in the oxyhydrogen flame, it emits a brilliant white light. When used as a paint it has the advantage over white lead of being uninjurious to the health of the users, and is not affected by hydrogen sulphide. It has the tendency, however, of being more liable to crack and peel off than the white lead paint. (U. S. P., pages 483, 492, and 554.)

139. Zinc Hydroxide.—Zinc hydroxide, $Zn(OH)_2$, is obtained as a gelatinous precipitate when caustic alkalies are added to solutions containing zinc; thus:



The precipitate dissolves in an excess of alkali, and, if this be not too great, is reprecipitated by boiling. Zinc hydroxide is readily decomposed by heat, thus:



140. Zinc Sulphide.—Zinc sulphide, ZnS , is found crystallized in nature, forming the mineral *sphalerite*, or *blende*. It is generally yellowish brown in color, has a resinous luster, and is translucent. It is precipitated from zinc solutions by alkali sulphides as a white precipitate, easily soluble in acids. The natural sulphide is easily converted into the sulphate by roasting it with free access of air.

141. Zinc Chloride.—Zinc chloride, $ZnCl_2$, is prepared in the laboratory by dissolving zinc in hydrochloric acid, or by acting on the metal with chlorine. If zinc is dissolved in hydrochloric acid and the solution is concentrated by evaporation, crystals having the composition $ZnCl_2 \cdot H_2O$ are deposited. If these are heated to expel the water, or if the original solution is evaporated to dryness, the chloride is partly decomposed with the formation of basic chloride, hydroxide, and oxide of zinc. The anhydrous chloride has a strong affinity for water and is sometimes used as a desiccating agent; it is a white,

granular powder, of specific gravity 2.9, melts at 262° C., and is soluble in water and alcohol. It is used on a large scale for the weighting of cotton goods, the preservation of timber and externally in medicine as a very reliable disinfecting medium. (U. S. P., pages 256, 491, 553, 554, and 618.)

142. Zinc Sulphate.—Zinc sulphate, $ZnSO_4$, crystallizes from an aqueous solution with 7 molecules of water as $ZnSO_4 \cdot 7H_2O$. The crystals are rhombic prisms. As with magnesium sulphate, 6 of these molecules of water are quite easily expelled by heat, while the seventh is only driven off with difficulty.

Zinc sulphate is prepared by dissolving zinc in sulphuric acid and, on a large scale, by the careful roasting of blende at a low red heat. It is known as *white vitriol*, is colorless, has an astringent, metallic taste, effloresces in dry air, and is somewhat soluble in water. It is frequently used in pharmacy, and for dyeing purposes. (U. S. P., page 494.)

143. Zinc Acetate.—Zinc acetate occurs as soft, white, six-sided, monoclinic plates with a pearly luster. Its odor is faintly acetous, and a dilute solution has a metallic taste.

The acetate may be produced by submitting zinc oxide to the action of acetic acid. (See U. S. P., page 489.)

144. Zinc Carbonate.—Zinc carbonate is a white, odorless, and tasteless powder; insoluble in water or in alcohol, but soluble in diluted acids.

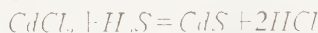
It is produced by the interaction of zinc sulphate and sodium carbonate, resulting in a solution of sodium sulphate with a precipitate of basic zinc carbonate. (See U. S. P., page 490.)

CADMIUM

Symbol Cd. Atomic weight 112.4. Molecular weight 112.4. Valence II.

145. History and Preparation.—Cadmium was discovered in 1817 by Hermann, and also by Strohmeyer, the latter giving to it the name *cadmium*, from *cadmia*, the ancient

name of *zinc ore*; it is generally found associated with zinc, and also as the sulphide in the mineral *greenockite*. It occurs as an impurity in commercial zinc, from which it is separated by dissolving the alloy in dilute hydrochloric acid and precipitating the cadmium as the sulphide, by passing hydrogen-sulphide gas through the solution. Zinc is not precipitated.



The cadmium sulphide so obtained is then dissolved in *hot, concentrated HCl* and ammonium carbonate is added to the solution, whereby cadmium carbonate is obtained; thus,



The cadmium carbonate is then purified by washing, dried, and strongly heated, the oxide being formed as follows:



Upon distilling the oxide with carbon, the metal is obtained; thus,



146. Properties.—Cadmium resembles zinc, its compounds being analogous to those of this metal, but it is whiter, heavier, and more easily volatilized and more fusible than this metal. It is ductile and malleable at ordinary temperatures, but becomes brittle at about 82°C ., and if bent when in this condition it crackles like tin. It has a specific gravity of 8.7 and melts at 320°C . It is not attacked by air, but acids act on it slowly. At a red heat it burns, producing brown fumes of cadmium oxide. Cadmium is used in the preparation of alloys of low melting point. (U. S. P., page 528.)

COMPOUNDS OF CADMIUM

147. Cadmium Oxide.—Cadmium oxide, CdO , may be obtained by calcining either cadmium carbonate or nitrate. Its color varies from yellowish brown to dark brown. It is reduced at high temperatures by carbon and by hydrogen, its reduction taking place more readily than that of zinc oxide.

148. Cadmium Sulphide.—Cadmium sulphide, CdS , occurs in nature as *greenockite* in the form of bright-yellow,

hexagonal prisms, terminated by six-sided pyramids. It is prepared in the laboratory by precipitating a solution of cadmium salt with hydrogen sulphide or a soluble sulphide, an amorphous precipitate of a fine yellow color being thus obtained.

149. Cadmium Iodide.—Cadmium iodide, CdI_2 , is obtained by digesting finely divided cadmium with iodine in the presence of water. It crystallizes from its aqueous solution in transparent, hexagonal prisms having a brilliant luster. It is soluble in water and alcohol; melts at $385^\circ C.$, and gives off iodine when heated to a higher temperature. Cadmium iodide, as well as cadmium bromide, $CdBr \cdot 4H_2O$, is used in photography.

150. Cadmium Sulphate.—Cadmium sulphate, $CdSO_4$, is obtained by dissolving either the metal, its oxide, or its carbonate in dilute sulphuric acid. It crystallizes with 8 molecules of water, $CdSO_4 \cdot 8H_2O$.

151. Cadmium Chloride.—Cadmium chloride, $CdCl_2$, crystallizes from solution of the metal or oxide in hydrochloric acid in rectangular prisms having 2 molecules of water. These readily effloresce in the air, lose water on heating, melt at $568^\circ C.$, and sublime at a higher temperature.

Cadmium differs from all other metals in forming a yellow sulphide insoluble in alkalies, so that its salts, mixed with excess of ammonia and treated with H_2S , give a yellow precipitate.

MERCURY

Symbol Hg. Atomic weight 200.6. Molecular weight 200.6. Valence I and II.

152. History and Occurrence.—Mercury has been known from the earliest times; its Latin name *argentum vivum*, of which the English name *quicksilver* is a literal translation, refers to its fluidity as well as to its color. The name mercury, from the planet of that name, was given by the alchemist to all volatile substances, but only this one has retained it.

The symbol of mercury, *Hg*, is derived from the Latin name *hydrargyrum*. It occurs native only sparingly, the chief ore being the sulphide, called *cinnabar*, which is found principally in Idria, Austria; Almaden, Spain; and New Almaden, California.

153. Preparation.—The process of extracting the mercury from its ore is a rather simple and easy one. It usually consists in roasting the ore in a reverberatory furnace, or even in a small blast furnace, with access of air, by which the sulphur is oxidized to sulphur dioxide, and the mercury set free and volatilized, according to the equation:



Sometimes lime or oxide of iron is mixed with the ore, and the sulphur retained in this way as sulphide of calcium or iron, depending on which has been used. The condensation of the vapors of mercury is, however, a matter of some difficulty, and the methods employed vary considerably in different localities.

At Idria, the vapors are passed through chambers and a series of twin tubes of cast iron cooled externally by water. They are so arranged that the condensed metal collects and runs down into the receptacle at the base of each tube. In Almaden, twelve parallel series of conical clay receivers, called *aludels*, luted together, are interposed between the furnace and its flue; each of these is about 20 inches long, and a series extends about 20 yards. The lines of aludels are of sufficient length to allow the vapors and gases to cool nearly to the temperature of the air, and so arranged as to allow the condensed mercury to gravitate toward a common channel where it collects.

154. Properties.—Mercury is a brilliant, silver-white metal. It has a specific gravity of 13.59 at 0° and is the only metal that is liquid at the ordinary temperatures. Cooled to -38.8° C., it solidifies to a malleable, tin-white mass, easily sectile, and crystallizing in regular octahedrons. Even at ordinary temperatures mercury has a small vapor tension, and gives off minute quantities of its vapor into the atmosphere in

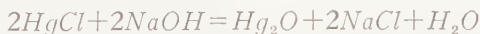
contact with it. It boils at 357°C ., yielding a colorless vapor of specific gravity 6.976. When heated almost to its boiling point in air, it becomes coated with the red oxide, HgO . It is unaltered in air; neither hydrochloric nor dilute sulphuric acid attacks it, but boiling, strong sulphuric acid, and even dilute nitric acid, dissolve it readily. Chlorine and sulphur unite directly with it.

Mercury is used in the arts for filling thermometers and barometers, and very extensively for extracting gold and silver from their ores. With most of the metals it forms alloys, known as *amalgams*; in some cases these amalgams possess a definite composition and crystalline form, for example, Hg_6Na is brittle and crystallizes in regular forms. Sodium amalgam is a convenient reducing agent, for when brought into contact with water or solutions in water, hydrogen is evolved. Tin amalgam is sometimes used for producing the silver coating on glass for mirrors.

Mercury forms two series of compounds, the mercurous, in which this metal is monovalent, and the mercuric, in which it is divalent. It will be seen that the two series differ very considerably in properties. (U. S. P., pages 219 and 220.)

COMPOUNDS OF MERCURY

155. Mercurous Oxide.—Mercurous oxide, Hg_2O , is a dark brown or black powder obtained by adding a solution of potassium or sodium hydroxides to a solution of a mercurous salt; thus,



It is very unstable, and is decomposed by the action of light or heat into mercuric oxide and metallic mercury.

156. Mercuric Oxide.—Mercuric oxide, HgO , may be prepared by either a dry or a wet method. The first consists in decomposing mercuric nitrate by heat; the salt is gradually heated in a flask in a sand bath until vapors cease to be disengaged. The oxide thus prepared is an orange-red, granular, and crystalline powder. It may also be prepared by heating

mercury in air for some time. By the wet method, mercuric oxide is prepared by decomposing a solution of a mercuric salt by potassium hydroxide, a yellow precipitate of mercuric oxide being thus obtained.

When mercuric oxide is heated, it assumes a dark-red color and decomposes, if the temperature is above 400° C., into oxygen and mercury. Mercuric oxide is soluble in acids, yielding mercuric salts. Hydroxides of mercury are unknown.

157. Mercuric Sulphide.—Mercuric sulphide, HgS , occurs in nature as the mineral cinnabar, both massive and in red rhombohedral crystals. It is obtained artificially by direct synthesis. The combination takes place when the elements are triturated in the cold, in the proportion of 100 parts of mercury and 18 parts of sulphur. A black mass is thus obtained that is sublimed in iron vessels. The black sulphide may be obtained also by treating a mercuric salt with H_2S . It becomes red when sublimed.

The pigment *vermilion* is a finely divided mercuric sulphide having a beautifully rich scarlet color. It is prepared by triturating for several hours, in a mortar, 300 parts of mercury and 114 parts of flowers of sulphur, and adding to the black sulphide thus obtained 75 parts of potassium hydroxide and 400 parts of water. The mixture is maintained at a temperature of about 45° C., being continually triturated with a pestle. As soon as the powder has acquired a fine scarlet color, it is rapidly washed with hot water and dried. It is employed in painting, coloring sealing wax, and for various other purposes.

158. Mercurous Chloride.—Mercurous chloride, $HgCl$, ordinarily called *calomel*, is precipitated whenever a chloride is added to a solution of a mercurous salt. It occurs in nature in tetragonal prisms in the mineral horn quicksilver. Commercially, it is prepared by subliming a mixture of mercuric sulphate, mercury, and salt:



The heavy yellowish-white powder that condenses is washed with water to remove any mercuric chloride. It is not soluble

in water, though chlorine water and nitric acid dissolve it by converting it into mercuric chloride. It sublimes between 400° and 500° C. without melting. Calomel is gradually decomposed by light, and is blackened by ammonium hydroxide. (U. S. P., page 215.)

159. Mercuric Chloride.—Mercuric chloride, $HgCl_2$, also known as *bichloride of mercury*, and as *corrosive sublimate*, is obtained by heating mercury in chlorine. It is manufactured by heating dry mercuric sulphate with an equal quantity of dry salt. A small amount of manganese dioxide is usually added to the mixture to prevent the formation of calomel. The mixture is placed in large glass vessels and heated, when the corrosive sublimate is converted into a vapor and condenses on the cooler part of the vessel in a white, transparent, or lustrous crystalline mass. It has an acrid, persistent, metallic taste, melts at 265° C., and sublimes at 300° C., and is somewhat soluble in water and in alcohol. It is used for the preservation of anatomical specimens, for dressing furs and skins, and as an antiseptic in surgery.

Mercuric chloride is a violent poison. Its antidote is the white of an egg, this forming an insoluble compound with the poison, thus rendering it inert to the stomach. Mercuric chloride unites with a number of other chlorides, forming readily soluble double salts. It also unites with mercuric oxide, forming oxychlorides.

160. Mercurous Iodide.—Mercurous iodide, HgI , is, as a rule, prepared by direct synthesis, 100 parts of mercury and 63.5 parts of iodine being triturated until the whole is converted into a green powder, which is then washed with boiling alcohol and dried. It may also be obtained by precipitating a mercurous salt with potassium iodide. Mercurous iodide is a rather unstable compound, being decomposed by light as well as by heat, the latter decomposing it into mercury and mercuric iodide. The same decomposition is affected by potassium iodide and the alkaline chlorides. (U. S. P., page 216.)

161. Mercuric Iodide.—Mercuric iodide, HgI_2 , is prepared by pouring a solution of 100 parts of potassium iodide

into a solution of 80 parts of corrosive sublimate, $HgCl_2$. A scarlet-red precipitate of mercuric iodide is thrown down. It is absolutely necessary that the compounds be mixed in exactly the proportions given; an excess of potassium iodide would dissolve the mercuric iodide first precipitated.

Mercuric iodide is nearly insoluble in water; it is slightly soluble in boiling alcohol, which deposits it, on cooling, in small, red, octahedral crystals.

On heating to $254^\circ C.$, mercuric iodide melts to a dark-yellow liquid that solidifies, when cooled, to a yellow mass. At $349^\circ C.$ the liquid boils and its vapor condenses in a dark-yellow liquid that solidifies to a yellow mass; at the same time, right rhombic prisms of a yellow color sublime. If these are rubbed with a glass rod or other hard substance, they instantly become red, first at the point of contact, then throughout the entire mass.

Mercuric iodide forms a compound with potassium iodide that is soluble in water. A solution of this potassium mercuric iodide is not precipitated by potassium hydrate, but the liquid rendered alkaline by the latter compound is a very sensitive test for ammonia (Nessler's test), with which it gives a precipitate or a brown cloud more or less intense, according to the quantity of ammonia present. (See also U. S. P., pages 220, 221, 268, 281, and 479.)

162. Sulphates of Mercury.—A *mercurous sulphate*, Hg_2SO_4 , and a *mercuric sulphate*, $HgSO_4$, are obtained by heating together mercury and sulphuric acid, the particular one formed depending on whether an excess of mercury or sulphuric acid, respectively, is used. The mercuric sulphate is the more important salt. It consists of white crystals that, on heating, undergo decomposition with the formation of mercurous sulphate. In presence of water the salt is very liable to become basic.

163. Nitrates of Mercury.—*Mercurous nitrate*, $HgNO_3$, and *mercuric nitrate*, $Hg(NO_3)_2$, are formed from mercury and nitric acid under similar conditions to the sulphates, and, like them, form basic salts in the presence of

water. For the weaker acids the affinity of mercury is too feeble to admit the formation of stable salts; the phosphates, carbonates, borates, and silicates have either not been prepared at all, or are obtained as basic compounds of variable composition.

INORGANIC CHEMISTRY FOR PHARMACY STUDENTS

(PART 6)

BORON AND ALUMINUM

BORON

Symbol B. Atomic weight 10.9. Molecular weight 10.9. Valence III.

1. History and Occurrence.—Boron occurs almost exclusively in the mineral kingdom, but it is claimed that it has been found in grape vines and in a few other plants. Under the Arabic name *buraq* (corrupted into borax), a salt obtained from certain lakes in Thibet, which contains boron as an essential constituent, it has been imported into Europe for a long time, and has been used in medicine, in working metals, and in imitating precious stones.

From this borax Homberg, in 1702, obtained boron trioxide, from which Davy, in 1807, by utilizing electricity, and Gay-Lussac and Thenard, in 1808, by chemical processes, obtained pure boron. Wöhler and Deville succeeded, in 1856, in crystallizing it. The mineral *sassolite* is *boric acid*, H_3BO_3 ; and *borax*, *boracite*, and *ulexite* are natural borates of sodium, magnesium, and calcium, respectively.

Boron is not found in the free state in nature but in combination, as *borax*, or *tincal*, $Na_2B_4O_7 \cdot 10H_2O$; *boracite*, $2Mg_3B_8O_{15} \cdot MgCl_2$; *borocalcite*, $CaB_4O_7 \cdot 4H_2O$; *natroborocalcite*, $Na_2B_4O_7 \cdot 2CaB_4O_7 \cdot 18H_2O$, and *sassolite*, or *boric acid*, H_3BO_3 .

2. Preparation and Properties.—Boron possesses two distinct forms—amorphous and crystalline. Amorphous boron is obtained by heating boron trioxide with potassium. The boron thus obtained is a greenish-brown powder, of specific gravity 2.45, that burns with a green flame at 700° C., and is a rather poor conductor of electricity. It is readily oxidized by nitric acid and is infusible at the temperature of the oxy-hydrogen flame.

The crystalline variety is obtained either by dissolving the amorphous modification in melted aluminum, when boron crystallizes out upon the aluminum cooling, or by melting boron trioxide and aluminum together and subsequently treating the mixture with hydrochloric acid to remove the impurities, such as aluminum and carbon, from the crucible. Boron crystallizes in short yellow or brownish-yellow quadratic octahedrons with a specific gravity of 2.65. The luster and hardness of crystallized boron is next to that of the diamond, and it will scratch both corundum and the ruby. The crystalline modification of boron is infusible and is insoluble in any acid. Aqua regia attacks it slowly. It is slowly soluble in melted caustic soda or potash.

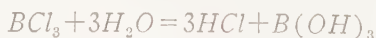
Heated to 410° C. in chlorine boron forms boron trichloride. Heated to redness, boron absorbs nitrogen, forming a white, infusible, insoluble powder of boron nitride, *BN*.

HALOGEN COMPOUNDS OF BORON

3. Boron Trichloride.—Boron trichloride, BCl_3 , may be obtained by heating crude amorphous boron in a current of chlorine, or by passing dry chlorine over a strongly heated mixture of boron trioxide and charcoal, according to the equation:



In a pure state, boron trichloride is a colorless, highly refractive liquid of specific gravity 1.35 at 17° C., boils at 12.5° C., and fumes in the air. It is readily decomposed by water into boric and hydrochloric acids:



4. Boron Tribromide.—Boron tribromide, BBr_3 , is obtained either by direct combination of its constituents or by passing bromine vapor over a heated mixture of charcoal and boron trioxide. It is a strongly fuming, colorless liquid, specific gravity 2.65, that boils at about 90° C. Its vapor is colorless, and it is decomposed by water the same as the trichloride.

5. Boron Trifluoride.—Boron trifluoride, BF_3 , was discovered by Gay-Lussac and Thenard in 1810. It is prepared by heating an intimate mixture of boric oxide and finely powdered calcium fluoride with sulphuric acid; the gas evolved is collected over mercury. The occurring reaction may be expressed by the equation:



Boron trifluoride is a colorless gas having an extremely suffocating odor; it fumes in the air and condenses to a liquid at -101° C.; it is decomposed by water, and must, therefore, be collected over mercury. Its affinity for water is so great that it carbonizes paper and certain organic substances in the same way as does strong sulphuric acid. Potassium and sodium burn brilliantly when heated in it.

The solution of boron fluoride in water is accompanied by a chemical reaction that is shown when the aqueous solution of this gas, saturated at ordinary temperatures, is cooled to 0° C., for crystals of boric acid are deposited, and a very acid liquid, *fluoboric acid*, HBF_4 , formed, according to the equation:



BORON AND OXYGEN

6. Boron Trioxide.—Boron trioxide, B_2O_3 , is formed whenever boron burns in air or oxygen. It is usually obtained by igniting boron hydroxide, or boric acid, $B(OH)_3$. A viscid mass is left, which solidifies to a colorless, transparent, and brittle glass having a specific gravity of 1.83. It unites readily with water, volatilizes at a white heat, and dissolves nearly all metallic oxides at a red heat.

7. Boric Acid.—Boric acid, $B(OH)_3$, or H_3BO_3 , was discovered by Homberg in 1702. It occurs free in nature in volcanic districts, as in Tuscany, where it issues, mixed with steam and gaseous matter, from fissures in the earth into natural or artificial little lakes or ponds, known as *lagoons*, or *lagoni*. The gases (*suffioni*) contain sensible traces of boric acid, which is dissolved by the water of the lagoni, which soon becomes charged with the acid; on evaporation this water furnishes the crude boric acid. Boric acid may be prepared from sodium borate or borax by dissolving it in boiling water, adding sulphuric acid, and allowing the whole to cool. The boric acid separates out in white, crystalline scales that are somewhat greasy to the touch and have a specific gravity of 1.43. They are soluble in 30 parts of water at $18^\circ C.$, and freely soluble in alcohol, the latter solution burning with a greenish flame. The aqueous solution of boric acid is feebly acid; it changes blue litmus solution to a wine color and turns turmeric paper brown. This constitutes the *normal* or *ortho-boric* acid. When heated to $120^\circ C.$, it loses 1 molecule of water and is converted into *metaboric acid*, HBO_2 . If the latter is maintained for some time at a temperature of $140^\circ C.$, it is converted into *tetraboric acid*, $H_2B_4O_7$, according to the equation:



Borax occurs naturally in the waters of certain lakes and marshes in California and Thibet. It is largely used as a flux in working metals. (U. S. P., pages 9, 384, and 476.)

ALUMINUM

Symbol Al. Atomic weight 27.1. Molecular weight 27.1. Valence III.

8. History and Occurrence.—Aluminum is one of the most abundant and, at the same time, most widely distributed constituents of the earth's crust. It derives its name from the word *alumen*, meaning alum. For a long time *alumina*, or *aluminum oxide*, was confounded with lime, from which it was first distinguished by Marggraf in 1754. In 1826 Oersted first

prepared the chloride, and Wöhler, in 1828, obtained the metal from this salt. This process was made a commercial one by St. Claire Deville in 1854. Aluminum does not occur free in nature. It is found, as nearly pure aluminum oxide, in *corundum*, *ruby*, and *sapphire*; in *diaspore*, $AlOOH$; in *bauxite*, $Al_2O(OH)_4$; in *feldspar*, $K_{12}Al_2SiO_6$; in *cryolite*, Na_3AlF_6 ; and as a silicate in all clays and in many minerals.

9. Preparation.—Aluminum was first produced commercially by the process invented by St. Claire Deville, which consists in reducing the chloride with sodium. By an improvement in this method sodium aluminum chloride, cryolite, and sodium are mixed together and heated in a furnace. A violent action takes place, great heat is evolved, and the liquefied mass of slag and metal gathers in the furnace. The latter is drawn off and cast into ingots. Tissier, at Amfreville, France, makes aluminum from the mineral cryolite, after a method proposed by H. Rose; and in the United States it is now produced in considerable quantities from the same mineral by electrolysis, a process devised by Hall.

The Hall electrolytic method for the preparation of aluminum has almost entirely superseded the other method mentioned. In this method pure anhydrous aluminum oxide is dissolved in a bath of fused cryolite and fluorspar in an iron pot lined with carbon which forms the cathode. The anode is composed of one or more carbon rods. The bath is kept at a temperature of about $1,000^{\circ}C$. By this process the aluminum oxide is reduced, the metallic aluminum falling to the bottom of the pot, while the oxygen unites with the carbon of the anode. The fluoride remains unchanged; hence, by frequently withdrawing the metal and renewing the aluminum oxide, the process is made continuous.

10. Properties and Uses.—Aluminum is a white metal with a somewhat bluish luster when polished. It crystallizes in octahedrons, and is a good conductor of heat and electricity. It is ductile, malleable, highly sonorous, and very light, its specific gravity being 2.5 to 2.7. It is less fusible than tin and zinc, but more so than silver, its fusing point being $657^{\circ}C$. It

requires a very high temperature to vaporize it. Like zinc, it is most easily rolled and bent between 100° and 150° C.

Aluminum is unaltered by the air, even by moist air. When heated in thin sheets in a current of oxygen, it burns and is converted into aluminum oxide. Nitric and sulphuric acid scarcely attack it. Hydrochloric acid dissolves it readily, disengaging hydrogen; it is also immediately attacked by boiling solutions of potassium or sodium hydrates, the hydrogen being disengaged and alkaline aluminates formed.

The remarkable lightness of this metal renders it extremely useful in the manufacture of beams of chemical balances, and of small weights, such as the decigramme, centigramme, and milligramme, since these weights when made of aluminum are more than three times as large as those of brass, and nearly nine times larger than when made of platinum; besides, the relative indestructibility of aluminum by the fumes of acids makes these weights still more valuable. The metal has also been lately used in the manufacture of cooking utensils, and especially of canteen vessels for military purposes, where, on account of its lightness and ability to resist vegetable acids, it has proved itself extremely useful. Aluminum, in the form of powder, is a powerful reducing agent, the combination with oxygen being accompanied by an enormous elevation of temperature. It can be used for reducing from their oxides metals—such as chromium and tungsten—that are difficult to reduce by other means. The great heat produced by burning aluminum powder is used for welding iron and steel. Probably the most important applications of metallic aluminum are as conductors of the electric current, in the preparation of various alloys, and more recently in the manufacture of aluminum cooking utensils. The chief impurities of the commercial aluminum are traces of iron and silicon.

COMPOUNDS OF ALUMINUM

11. Aluminum Oxide.—Aluminum oxide, Al_2O_3 , generally known as *alumina*, occurs in nature in the mineral *corundum*, which includes the precious stones known as the

ruby and *sapphire*, as well as the valuable polishing material called *emery*, distinguished by its extreme hardness, in which it ranks next to the diamond. It may be prepared by the combustion of the metal in oxygen or by igniting the hydrate. Fusion with potassium bisulphate or with caustic potash renders it soluble in acids.

12. Aluminum Hydroxide.—Aluminum hydroxide, $Al(OH)_3$, occurs in nature as *hydrargillite*, or *gibbsite*, or as *diaspore*, $AlOOH$. These two modifications are crystalline. It is prepared by adding ammonium hydrate to the solution of a salt of aluminum, when a gelatinous precipitate separates. This is nearly insoluble in an excess of ammonium hydrate, but is readily soluble in potassium and sodium hydroxides. When washed and dried, the gelatinous hydrate shrinks very much, and forms a mass resembling gum.

Aluminum hydroxide may be used in the preparation of *lakes*, which are insoluble colored compounds made by precipitating dyestuffs from their solutions by the addition of aluminum hydroxide. It and aluminum acetate are also used as *mordants* in dyeing. The fabric to be dyed is first treated with aluminum hydroxide or acetate and then with a solution of the dye, which is precipitated upon the cloth as an insoluble compound. (U. S. P., page 41.)

13. Aluminum Chloride.—Aluminum chloride, $AlCl_3$, sometimes written Al_2Cl_6 , is prepared by passing over an incandescent mixture of alumina and charcoal a current of chlorine, aluminum chloride and carbon monoxide being formed according to the equation:

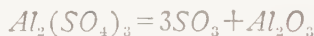


The aluminum chloride thus obtained is a white, semi-crystalline, waxy substance, having sometimes a light-yellow color; it is fusible, and volatilizes in the air at a temperature slightly above 100° C. When exposed to the air, aluminum chloride gives off white fumes and readily attracts moisture. It dissolves in water with the production of heat. A solution of aluminum chloride may be obtained by dissolving gelatinous alumina in hydrochloric acid. When this solution is evapo-

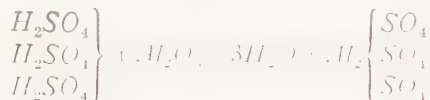
rated, it decomposes as soon as it attains a certain degree of concentration, disengaging hydrochloric acid and leaving aluminum oxide. Aluminum chloride readily combines with sodium chloride, forming a double chloride, $NaAlCl_4$.

Authorities differ as to the molecular weight of aluminum chloride, but recent experiments tend to show that at high temperatures or when taking part in chemical reactions the formula is $AlCl_3$, while at lower temperatures it is Al_2Cl_6 .

14. Aluminum Sulphate.—Aluminum sulphate, $Al_2(SO_4)_3$, is obtained by dissolving aluminum hydrate in dilute sulphuric acid. It crystallizes with difficulty in needles and in thin pearly scales, in which state it contains 18 molecules of water of crystallization; it dissolves in 2 parts of cold water, and has a sweet, astringent taste. When slowly heated, it first loses its water of crystallization until at a higher temperature it gives off sulphur trioxide, leaving a residue of alumina, according to the equation:



Aluminum sulphate represents 3 molecules of sulphuric acid, in which the 6 atoms of hydrogen have been replaced by 2 atoms of aluminum, thus:



It is used as a mordant in dyeing, for the treatment of sewage, and for weighting of paper.

15. Alum.—Aluminum and potassium double sulphate, more generally known as *alum*, $AlK(SO_4)_2 \cdot 12H_2O$, is obtained as a crystalline deposit by adding to a concentrated solution of potassium sulphate a concentrated solution of aluminum sulphate, and stirring the mixture well with a glass rod. It is only sparingly soluble in cold water, but dissolves more easily in hot, and quite abundantly in boiling water, being deposited from the latter, on cooling, in voluminous, transparent octahedrons, and has a specific gravity of 1.7. When heated, these crystals melt in their own water of crystallization;

in losing this water the melted mass swells considerably. (U. S. P., pages 39 and 40.)

16. Ammonium Alum.—Ammonium alum is obtained by adding ammonium sulphate to a solution of aluminum sulphate. It possesses a composition analogous to that of ordinary alum, with which it is isomorphous. Its formula is $AlNH_4(SO_4)_2 \cdot 12H_2O$. It is very often substituted in the arts for potassium alum, being cheaper than the latter. When strongly calcined, it leaves a residue of pure alumina.

Other alums are known, in which iron, manganese, and chromium play the part taken by aluminum in ordinary alum. The most important of these compounds are: *Manganese alum*, $MnK(SO_4)_2 \cdot 12H_2O$; *iron alum*, $FeK(SO_4)_2 \cdot 12H_2O$; *chrome alum*, $CrK(SO_4)_2 \cdot 12H_2O$. It is seen that each of these presents an atomic composition similar to that of ordinary alum.

17. Mineral Silicates of Aluminum.—The silicates of aluminum occur in combination with silicates of other elements in large quantities in the crust of the earth. Aluminum is very frequently replaced by iron in the form of Fe_2O_3 , thus rendering the chemical formulas of these minerals rather complicated. The chief silicates of aluminum are: *Topaz*, $Al_2SiO_4F_2$; *garnet*, $(Mg \cdot Fe)_3Al_2Si_3O_{12}$; *orthoclase*, $Al(Si_3O_8)K$; *kaolin*, $H_2Al_2Si_2O_8 \cdot H_2O$; and *albite*, $NaAl(Si_3O_8)$.

TIN, LEAD, VANADIUM, AND CHROMIUM

TIN

Symbol Sn. Atomic weight 118.7. Molecular weight 118.7. Valence II and IV.

18. History and Occurrence.—Tin has been known for many thousands of years; it is spoken of by Moses (Numbers xxxi, 22), and Homer mentions it in his Iliad. Much of the brass of the ancients was an alloy of copper and tin; as the latter was obtained from Cornwall, England, Herodotus speaks of the British Isles as the *tin islands*. The principal ore of tin is *stannic oxide*, known as the mineral *cassiterite*, or *tinstone*; it occurs in veins running through rocks, and also in the beds of streams, from the disintegration of these rocks. It is found principally in Cornwall, England, and Banca and Malacca, and also, though less abundantly, in New Hampshire and in California.

19. Preparation.—In the process adopted at the Cornish plants the tinstone is stamped to crush it and is then freed from gangue by washing. The tinstone, being extremely hard, is not reduced to so fine a powder as the other minerals mixed with it, and the high specific gravity of the stannic oxide, which is 6.5, as against that of sand or quartz, which is 2.7, makes the separation by water easy and complete. After being washed, the ore is roasted in a revolving or reverberatory furnace to drive off any arsenic or sulphur that may remain in the ore. The ore is again washed after the roasting to remove the ferric oxide. The purified tin oxide, which contains between 60 and 70 per cent. of tin, is intimately mixed with about one-fifth of its weight of anthracite coal, and a small quantity of lime or fluorspar, to form a fusible slag with the silicious impurities, and reduced in a reverberatory furnace.

The impure tin obtained is cast into molds and refined by the process known as *liquation*.

20. The impure tin obtained is purified by placing the ingots in a reverberatory furnace and gradually raising the temperature to the fusing point of tin. The pure tin, being more easily fusible, melts and flows into a cast-iron basin, while the less fusible portion, an alloy of tin, iron, arsenic, and usually copper, remains as dross on the hearth of the furnace. The metal in the cast-iron basin is kept in a molten condition, and is stirred, or *poled*, with a pole of green wood. This operation may last from one to several hours, depending on the grade of tin desired. The dross separating during this operation and the residue, or *hardhead*, remaining on the hearth are afterwards recharged into the smelting furnace.

The purified tin is ladled into ingots and is known commercially as *block tin*. *Grain tin* is prepared by heating block tin until the metal becomes crystalline when, owing to its brittle nature, it is broken up with hammers or allowed to fall from a height.

The purest of commercial tins is that imported from Banca, known as *Banca tin* or *Straits tin*. Next in purity is the English tin.

21. Properties.—Tin is a brilliant-white metal that does not tarnish in the air, and has a specific gravity of 7.29. It is dimorphous, crystallizing in forms belonging to the quadratic and isometric systems. It is quite malleable and may be beaten into very thin leaves; at 100° C. it is ductile and can be drawn into wire. It possesses little tenacity. It crackles when a bar of it is bent, producing that peculiar noise known as the “cry of tin.” It possesses a peculiar odor, and is a good conductor of heat and electricity. Its melting point is about 232° C.; and it distils at a white heat. Heated in air, it burns readily to oxide, though it retains its luster in air at ordinary temperature. It is readily attacked by acids, and dissolves in aqueous solutions of the alkalies.

22. Uses.—Tin is largely used in the arts for making tin-foil, for plating iron, in the manufacture of tin plate, and also

as a constituent of many important and valuable alloys. With copper it forms gun metal, speculum metal, bell metal, and bronze; with lead it forms solder and pewter. Britannia metal is an alloy of tin, antimony, and copper; alloyed with mercury, tin yields an amalgam that is used for producing the bright reflecting surface on glass mirrors. (U. S. P., page 553.)

COMPOUNDS OF TIN

23. Stannic Chloride.—Stannic chloride, SnCl_4 , known to the alchemists in the middle ages as *liquor fumans Libavii*, may be obtained by the direct action of chlorine gas on tin. It is a colorless, fuming, caustic liquid that boils at 114°C . It readily unites with water, evolving heat, and forming several crystalline hydrates. With alkali chlorides it forms definite compounds, the potassium salt being K_2SnCl_6 . It is used in dyeing.

24. Stannous Chloride.—Stannous chloride, SnCl_2 , is prepared by dissolving tin in hydrochloric acid. If the solution is made strong enough, some of the salt will crystallize out with 2 molecules of water, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. This salt is largely used in dyeing, and is known in commerce as *tin salt*. Stannous-chloride crystals dissolve readily in water. If there is but little water present the solution is perfectly clear, but if much water is added the solution becomes turbid, owing to the formation of the basic chloride, SnOHCl . The atmospheric oxygen dissolved in water also takes part in this decomposition of stannous chloride, from which it removes part of the metal, a corresponding quantity of stannic chloride being formed.

Stannous chloride reduces many oxygenized and chlorinated compounds, and is largely used in the laboratory. It decomposes the salts of silver and mercury, setting free the metal. It instantly decolorizes the purple solution of potassium permanganate. (U. S. P., page 551.)

25. Stannic Oxide.—Stannic oxide, SnO_2 , is found in nature as the mineral *cassiterite*, or *tinstone*, in the form of beautiful, hard, transparent crystals of a yellowish-brown color.

It may be prepared by burning the metal in air or by igniting either of the hydrates. It is obtained as a white powder, of specific gravity 6.6, that is insoluble in all acids except hydrofluoric. Owing to its hardness, it is used for polishing glass under the name of *putty powder*. When fused with alkali hydrates, it forms *stannates*.

26. Stannic Acids.—When a solution of stannous chloride in water is boiled, or a solution of a stannate is treated with just enough acid to decompose it, a white precipitate is formed, known as **stannic acid**, H_2SnO_3 . It dissolves readily in acids and in alkali hydrates.

When metallic tin is treated with nitric acid, a white powder is obtained that also has the composition H_2SnO_3 , but is insoluble in acids and differs in physical and chemical properties widely from the stannic acid; the name **metastannic acid** is given to this modification.

27. Stannous Oxide.—Stannous oxide, SnO , is of little practical importance. It is obtained by heating stannous oxalate in a closed vessel, and is a black, crystalline powder that is combustible in air. If water is added to SnO , a hydrate is formed that gradually absorbs oxygen from the air, and passes into stannic acid. With sulphuric acid it forms stannous sulphate, $SnSO_4$.

28. Sulphides of Tin.—*Stannous sulphide*, SnS , is obtained by leading hydrogen sulphide through a stannous solution. It is a dark-brown or black precipitate that dissolves in polysulphides of the alkalies with the formation of alkali sulphostannates.

Stannic sulphide, SnS_2 , may be obtained either in the amorphous or crystalline form. By leading hydrogen sulphide through a solution of stannic chloride, stannic sulphide is obtained as a yellow amorphous precipitate. By heating a mixture of tin filings, sulphur, and ammonium chloride, or, better, tin amalgam, sulphur, and dry ammonium chloride, stannic sulphide is obtained as a golden-yellow crystalline powder, known as *mosaic gold*. In this form it is used as a pigment, especially for bronzing.

LEAD

Symbol Pb. Atomic weight 207.2. Molecular weight 207.2. Valence II and IV.

29. History and Occurrence.—Lead is one of those metals that have been known from the earliest ages of history; it is frequently mentioned in the Old Testament and other sacred writings. The Romans worked the lead ores of Spain and of England, and the Carthaginians those of Spain, the extent of their mining and smelting operations exciting surprise, even at the present day. The principal workable ore of lead is its sulphide, *galenite*, more popularly known as *galena*, PbS , though it occurs also somewhat abundantly as *carbonate*, or *cerussite*; as *sulphate*, or *anglesite*; as *chloroarsenate*, or *minetite*; as *chlorophosphate*, or *pyromorphite*; and in sundry other forms.

30. Preparation.—The reduction of lead from its ores is a comparatively simple metallurgical process. The method most generally adopted at the present time is to reduce the lead in blast furnaces. This method is suitable for ores containing lower percentages of lead than are necessary for other processes, and also for other ores containing gold and silver as well. Ores containing considerable sulphur are roasted and the roasted ore mixed with silicious and basic ores containing gold, silver, and small amounts of lead, copper, arsenic, antimony, iron, and bismuth. This mixture of ores is then charged into the blast furnace together with coke and limestone. The slag from a blast furnace usually contains from 30 to 40 per cent. silica, 30 to 40 per cent. iron, and 15 to 25 per cent. lime. The sulphur remaining in the ore unites with the iron and copper to form *matte*, which is an artificial sulphide, and the gold, silver, and lead are collected together. The matte is recharged with fresh ore. From time to time the lead, silver, and gold mixture is tapped into pots and transferred to a *drossing kettle*.

In the drossing kettle the molten metal is allowed to cool until it begins to harden on the edges, when the greater portion of the copper, arsenic, antimony, iron, and bismuth rise to the

surface and are skimmed off. After having been thoroughly drossed, the temperature of the kettle is raised, the metal, or *base bullion*, is run in pigs, and sent to the refinery, where the gold and silver are separated from the lead.

31. Desilverizing Lead.—Among the many processes devised for the purpose of desilverizing the lead the best known are the Pattinson, the Rozan, and the Parkes processes.

The *Pattinson process* depends on the fact that pure lead solidifies at a somewhat higher temperature than an alloy of silver and lead. By melting the lead and then allowing it to cool, the purer lead crystallizes out first; if this is removed by a perforated ladle, the liquid remaining is richer in silver. By repeating this treatment the silver accumulates, until a ton of the lead contains as much as 600 to 700 ounces of silver, after which the silver is best separated by *cupellation*.

32. Cupellation.—For obtaining the silver free from lead, the metal is heated in an oxidizing atmosphere on a *cupel*, that is, in a special furnace, the bed of which is made of bone ash impregnated with pearl ash. The lead is oxidized to litharge, which collects at the surface of the charge and is blown off or is to some extent absorbed by the bed of the furnace, carrying with it the impurities and leaving molten silver.

33. Properties.—Lead is a soft, brilliant, bluish-white metal that leaves on paper a bluish-gray streak, is very malleable and slightly ductile, and tarnishes in the air. It has a specific gravity of 11.37, crystallizes in regular octahedrons, fuses at 328° C., and volatilizes at a bright-red heat. At a white heat it may be distilled. It has but a feeble tenacity, a wire 2 millimeters in diameter sustaining only a weight of 9 kilogrammes. Its freshly cut surface remains bright in perfectly dry air and also in water free from air.

When melted in the air, lead is rapidly converted into the oxide. It is scarcely attacked by sulphuric or hydrochloric acid at ordinary temperature, but dissolves readily in nitric acid. In presence of air and moisture it is acted on by quite feeble acids, such as acetic and carbonic acids; hence, the use of vessels made of lead or soldered with lead should be

avoided for cooking vegetables, fruit, etc., which all contain more or less acid. When taken into the system, lead unites definitely with certain tissues and is retained there, until finally sufficient accumulates to produce poisoning. Acute colic is characteristic of poisoning by a large dose of lead, but in chronic poisoning, which is far more common, there is paralysis, particularly in the muscles of the forearm, causing the wrist to drop; or there may be simply an indefinable feeling of malaise, accompanied by dyspeptic symptoms.

34. Uses of Lead.—Lead is largely used in the manufacture of pipes for the distribution of water and gas, and, mixed with a small portion of arsenic, in the manufacture of shot. When reduced to sheets it is made into gutters, the covering of roofs, and lining for troughs and reservoirs. Alloyed with antimony and tin, it forms type metal; with bismuth, the soft alloy is used for permanent pencil points; with tin, it makes pewter and soft solder; and with tin, cadmium, and bismuth, a fusible metal which melts at 60° C.

COMPOUNDS OF LEAD

35. Lead Oxide.—Lead oxide, PbO , occurs in nature as the mineral *massicot*. It is prepared on a large scale in the arts under the name of *litharge*, by heating melted lead in a current of air. Its color is either pale yellow or orange yellow, according to the temperature at which it is prepared. Its specific gravity varies from 8.74 to 9.50. Acids dissolve it very readily, forming definite salts. Litharge is soluble in alkali-hydroxide solutions as well as in lime water. It is employed in the manufacture of glass, of lead acetate, and of white lead. It gives to linseed oil drying properties. (U. S. P., page 329.)

36. Lead Hydroxide.—Lead hydroxide, $Pb(OH)_2$, is known only as a colorless, sweetish liquid, obtained by the action on lead of water and air, free from carbon dioxide. The precipitate produced by hydroxides of the alkalis in lead solutions is usually a compound having the composition $Pb_2O(OH)_2$.

37. Lead Peroxide.—Lead peroxide, PbO_2 , is obtained as a brown powder by treating *minium*, or *red lead*, with dilute nitric acid and washing the precipitate with boiling water. Lead peroxide is insoluble in water; it is readily decomposed by heat, losing half its oxygen and being converted into lead oxide. It is an energetic oxidizing agent. When it is briskly triturated with sulphur, the latter is ignited. If it is introduced into a test tube with sulphur dioxide, the latter is immediately absorbed, with formation of lead sulphate:



(U. S. P., page 536)

Digested with ammonium hydroxide, it forms water and lead nitrate; it sets iodine free from potassium iodide, and bleaches a solution of sulphindigotic acid. It combines directly with the oxides of potassium, sodium, calcium, and even lead, forming salts called *plumbates*, having the general formula M_2PbO_3 , in which *M* stands for a univalent metal.

38. Lead Sesquioxide.—Lead sesquioxide, Pb_2O_3 , is obtained as a reddish-yellow powder, by mixing lead acetate and sodium hydroxide, and adding sodium hypochlorite to this solution.

39. Red Lead.—Red lead, or *minium*, Pb_3O_4 , is obtained by gently heating lead oxide in the air, thus causing it to take up oxygen. It is a mixture of $2PbO$ and PbO_2 but the commercial article varies somewhat in composition, and its color varies slightly according to the method of preparation. It is used as a pigment, and sometimes as a flux in the manufacture of glass, porcelain, etc. It is soluble in glacial acetic acid and in hydrochloric acid.

40. Lead Sulphide.—Lead sulphide, PbS , occurs as *galena* in nature in beautiful cubical crystals of a bluish-gray color and a metallic luster; its specific gravity is 7.25 to 7.70. It melts at red heat. When heated in contact with air, it is converted into oxide and sulphate, and, by the action of an excess of sulphide on these compounds, metallic lead is produced. Hot, fuming nitric acid converts lead sulphide into

sulphate. Concentrated and boiling hydrochloric acid transforms it into chloride, with evolution of hydrogen sulphide. Lead sulphide is obtained as a black precipitate by leading hydrogen sulphide into a lead solution; it is prepared also by fusing lead and sulphur together.

41. Lead Chloride.—Lead chloride, $PbCl_2$, has been found in the crater of Vesuvius after an eruption, and is known as *cotunnite*. It is precipitated from any lead solution, if sufficiently concentrated, on the addition of hydrochloric acid or a chloride. It is a heavy, white powder, soluble in 135 parts of cold or 30 parts of boiling water, from which it crystallizes, on cooling, in lustrous needles. It melts when heated in closed vessels, and at a higher temperature sublimes. The fused lead chloride is translucent and sectile, and is known as *horn lead*. White and yellow oxychlorides are used as pigments, variously known as *mineral yellow*, *Turner's yellow*, and *Cassel yellow*.

42. Lead Tetrachloride.—Lead tetrachloride, $PbCl_4$, is formed by passing chlorine into concentrated hydrochloric acid containing lead chloride, until it is saturated, and then adding ammonium chloride, when yellow crystals of $PbCl_4 \cdot 2NH_4Cl$, or $Pb(NH_4)_2Cl_6$, separate. When treated with ice-cold sulphuric acid, these crystals are decomposed into hydrochloric acid, ammonium sulphate, and lead tetrachloride, the latter separating as an oily liquid. Lead tetrachloride crystallizes at $-15^\circ C.$, has a specific gravity of 3.18, and is decomposed into chlorine and the dichloride at ordinary temperature. At $105^\circ C.$ it decomposes with explosive violence.

43. Lead Iodide.—Lead iodide, PbI_2 , is obtained as a beautiful yellow precipitate when a solution of potassium iodide is added to a solution of a lead salt. This compound melts to a red-brown liquid at a high temperature. Lead iodide is soluble in 1,235 parts of cold or 194 parts of boiling water. Upon cooling a boiling, saturated solution, lead iodide is deposited in golden-yellow scales, which have a magnificent luster.

44. Lead Nitrate.—Lead nitrate, $Pb(NO_3)_2$, is prepared by dissolving lead, or its oxide or carbonate, in dilute nitric acid, from which it crystallizes in white, regular octahedrons. The crystals dissolve in $7\frac{1}{2}$ times their weight of cold water, and in a much less quantity of boiling water. At a red heat this salt is decomposed into nitrogen peroxide, oxygen, and lead oxide. It has an astringent taste, and decrepitates when heated. It is used in the manufacture of matches, in dyeing, and for the preparation of other lead salts.

45. Lead Sulphate.—Lead sulphate, $PbSO_4$, occurs in nature in rather small amounts. It is obtained as a heavy white precipitate by adding sulphuric acid or a soluble sulphate to a solution of a lead salt. It is practically insoluble in water, but dissolves slightly in strong sulphuric acid; nitric and hydrochloric acids dissolve it somewhat more freely. It dissolves readily in some ammonium salts, as the tartrate and acetate. It melts at a red heat without undergoing decomposition. It is used in the preparation of rapidly drying oil varnishes, and frequently as a pigment in place of white lead.

46. Lead Carbonate.—Lead carbonate, $PbCO_3$, or basic carbonates of variable composition are precipitated when sodium carbonate is added to a solution of lead nitrate. The basic carbonate known as *white lead* is of great importance as a white pigment. If a solution of lead acetate is boiled with lead oxide and then filtered, a basic acetate is obtained, and on passing carbon oxide through the solution a white precipitate of this basic carbonate, $2PbCO_3 \cdot Pb(OH)_2$, is deposited. Prepared in this way, however, the pigment is denser and does not possess the same covering power as that formed more gradually by the so-called *Dutch process*. In this process coils of sheet lead are placed in conical earthenware vessels, resting on a ledge, the bottom of the vessel containing weak acetic acid. These vessels, which are about 8 inches high, are stacked in layers, which are covered with tan bark or other fermenting vegetable matter; these stacks are about 15 feet square and 20 feet high. The heat generated by the fermentation gradually volatilizes the acetic acid and brings it into contact with

the lead, and at the same time the carbon dioxide formed during the fermentation reacts with the basic acetate, yielding the basic lead carbonate. The acetic acid is then free to act on a further portion of lead, and the process repeats itself until practically the whole of the lead is transformed into *white lead*.

47. Lead Chromate.—Lead chromate, $PbCrO_4$, is found crystallized in nature, constituting the mineral *crocoisite*. It is obtained as a yellow precipitate by adding potassium chromate to the solution of a lead salt. Lead chromate gives up oxygen readily when heated in the presence of oxidizable substances. It dissolves quite readily in solutions of alkali hydroxides. It is used as a pigment under the name of *chrome yellow*, and is sometimes employed as an oxidizing agent in the analysis of organic substances.

NOTE.—Additional information on lead salts is found in the U. S. P., pages 135, 249, 250, 326, 328, and 620.

VANADIUM

Symbol V. Atomic weight 51. Molecular weight 51. Valence I, II, III, IV, and V.

48. Occurrence and Preparation.—Vanadium occurs in nature in the form of vanadates, which are analogous to phosphates. It has been found in clay, coal, and some rare minerals. Its principal minerals are *vanadinite*, $3Pb_3V_2O_5 \cdot PbCl_2$; *dechenite*, $PbVO_3 \cdot ZnVO_3$; *descloisite*, $Pb_2V_2O_7$; and *mottramite*, $(CuPb)_5V_2O_{10} \cdot 2H_2O$. Metallic vanadium may be obtained by fusing the ore with sodium nitrate; *sodium vanadate* is thus formed which is soluble in water. Upon treating the water solution with an ammonium salt, an orange-colored precipitate of *ammonium metavanadate*, NH_4VO_3 , is formed, which, upon being heated, is converted into *vanadium pentoxide*, and the oxide, when heated with carbon, is reduced to the metal.

49. Properties.—Vanadium is a grayish-white, non-magnetic powder having a specific gravity of 5.5. It is neither fusible nor volatile when heated in hydrogen. Heated in

oxygen it burns with a brilliant display of sparks, forming the oxide. It is insoluble in hydrochloric acid, and is only slowly soluble in strong, hot sulphuric acid. Metallic vanadium is harder than steel and precipitates platinum, gold, and silver from solutions of their salts. It is largely used in the manufacture of steel and steel alloys.

50. Compounds of Vanadium.—The *oxides* of vanadium recall those of nitrogen; they are: the *suboxide*, V_2O ; *dioxide*, V_2O_2 ; *trioxide*, V_2O_3 ; *tetroxide*, V_2O_4 ; and *pentoxide*, V_2O_5 . With chlorine, vanadium forms the compounds VCl_2 , VCl_3 , and VCl_4 . The vanadates are derived from ortho-, meta-, and pyro-vanadic acids, which are similar to the acids of phosphorus in structure. Of these, the *metavanadates* are the most stable. These are derived from the acid HVO_3 , which is a golden-yellow compound sometimes used in place of gold bronze.

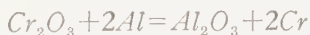
Orthovanadic acid, H_3VO_4 , is the final product of the oxidation of vanadium.

CHROMIUM

Symbol Cr. *Atomic weight* 52. *Molecular weight* 52.
Valence II, III, and VI.

51. History and Occurrence.—Chromium was discovered in 1797 by Vauquelin, in a mineral from Siberia, known as *crocoisite*, which is a chromate of lead. It derives its name from a Greek word meaning "color," in allusion to the varied colors of its compounds, on which their uses in the arts largely depend. It occurs in nature in the mineral *chromite*, $FeO \cdot Cr_2O_3$, or *chrome iron*, a combination of chromium oxide and ferrous oxide.

52. Preparation and Properties.—Chromium may be obtained by mixing chromic oxide with powdered aluminum and igniting the mixture, the following reaction taking place:



Chromium is a light-gray, or tin-white, lustrous, crystalline substance. It is very hard and difficult to fuse, and oxidizes

very slowly when heated in the air, but heated in oxygen or in the oxyhydrogen flame, it burns to chromic oxide, Cr_2O_3 . It is insoluble in nitric acid, but dissolves in hydrochloric and hot sulphuric acids. Its specific gravity is 6.81, and its melting point is $1,520^{\circ} C$. It is non-magnetic. Large quantities are used in the form of an alloy, *ferrochrome*, containing between 60 and 70 per cent. of chromium. These ferrochromes are used to introduce chromium into steel, thereby greatly increasing the hardness of the steel.

COMPOUNDS OF CHROMIUM

53. Hydroxides of Chromium.—*Chromous hydroxide*, $Cr(OH)_2$, is obtained as a light-brown precipitate when potassium hydroxide is added to a solution of chromous chloride. It readily gives up water and hydrogen and is converted into *chromic oxide*, Cr_2O_3 .

Chromic hydroxide, $Cr(OH)_3$, is obtained as a light-blue precipitate by adding ammonia to a solution of a chromic salt, and carefully drying in a vacuum the precipitate thus formed. When heated, this decomposes first into $CrOOH$ and finally into Cr_2O_3 . Sodium and potassium hydroxides dissolve chromic hydroxide with the formation of the corresponding chromites, which are derivatives of the acid $CrOOH$. When solutions containing these chromites are boiled, chromic hydroxide is precipitated, but this precipitate always contains some of the alkali metal in combination.

54. Chromic Oxide.—Chromic oxide, or chromium sesquioxide, Cr_2O_3 , may be prepared by heating either of the hydroxides, but is more readily obtained on a large scale by heating a mixture of potassium dichromate and sulphur, when potassium sulphate and chromic oxide result. Obtained in this way, it is a green powder that becomes almost insoluble in acids when heated. It is used in coloring glass and in china painting.

55. Chromium Trioxide.—Chromium trioxide, CrO_3 , may be prepared by treating a concentrated solution of an alkali chromate or dichromate with concentrated sulphuric acid,

when the trioxide crystallizes from the solution in fine red needles. It is deliquescent, and when dissolved in water gives an acid solution, which, when neutralized, yields chromates, thus indicating that the solution contains chromic acid, H_2CrO_4 . When heated, the trioxide gives up half its oxygen and is converted into chromic oxide. It is a powerful oxidizing agent and is reduced by almost any oxidizable substance.

56. Chromous Chloride.—Chromous chloride, $CrCl_2$, may be obtained by reducing chromic chloride by hydrogen at a moderate heat. It is a white, crystalline substance, soluble in water, forming a blue solution that, by absorption of oxygen, rapidly changes its color to green.

57. Chromic Chloride.—Chromic chloride, $CrCl_3$, is the most important compound of chromium and chlorine. It may be obtained by passing chlorine gas over an ignited and perfectly dry mixture of chromium and charcoal. A sublimate of brilliant, peach-blossom-colored scales is thus obtained, which is almost insoluble in cold and only sparingly soluble in boiling water, forming with the latter a green solution.

It may be prepared in solution by dissolving chromic hydroxide in hydrochloric acid. This solution has a deep green color, and when sufficiently concentrated deposits crystals having the composition $CrCl_3 \cdot 6H_2O$. When these crystals are heated in the air, they are decomposed with the formation of chromic oxide, but if heated in an atmosphere of chlorine or hydrochloric acid the water is expelled and the reddish-violet anhydrous chloride remains. This dissolves in water, forming a green solution, but if first sublimed it becomes almost insoluble in water and acids. With the chlorides of the alkalies it forms double salts, as examples of which may be mentioned $KCrCl_4$ and K_2CrCl_6 .

58. Chromium Oxychloride.—Chromium oxychloride, or **chromyl chloride**, CrO_2Cl_2 , is obtained by heating a previously fused mixture of common salt and potassium dichromate with sulphuric acid; abundant red vapors are disengaged, and condensed to a blood-red liquid. It boils at $116.8^\circ C$. On

contact with water it decomposes into hydrochloric acid and chromic acid.

59. Chromium Sulphate.—Chromium sulphate, $Cr_2(SO_4)_3$, may be prepared in solution by dissolving chromic hydroxide in sulphuric acid. If the solution is allowed to evaporate slowly, it will deposit the sulphate in purple crystals having the composition $Cr_2(SO_4)_3 \cdot 15H_2O$, but if the solution is first boiled it turns green and the sulphate will not crystallize from it. If, however, the green solution is allowed to stand for some time it becomes purple again and purple crystals of sulphate separate. It appears to be true of the solutions of chromium salts in general that they exist in two modifications: a purple modification from which crystals are readily obtained, and a green variety, obtained by boiling the purple form, from which crystals cannot be obtained. The green solution changes back to purple if allowed to stand for some time.

60. Chrome Alum.—Like aluminum sulphate, chromium sulphate combines with the sulphates of the monovalent metals, forming double sulphates that crystallize from solution with 12 molecules of water. The most important of these, the double sulphate of chromium and potassium, known as **chrome alum**, has the formula $CrK(SO_4)_2 \cdot 12H_2O$. It is prepared by reducing a solution of potassium dichromate containing sulphuric acid, by means of sulphur dioxide. Neglecting the water of crystallization, which is furnished by the solution, the equation representing its formation may be written:



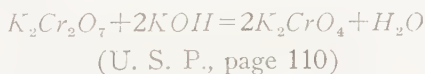
Chrome alum is used in tanning and dyeing, and to a slight extent in photography.

61. Chromic Acid and Chromates.—Chromous compounds when exposed to the air or treated with oxidizing agents, are readily oxidized to chromic compounds, which is the limit of oxidation if an acid is present. In these compounds chromium acts as a base and is usually regarded as such. If, however, the oxidation is carried out in the presence

of a strong base, it proceeds further, and a chromate results. In these compounds chromium plays the part of an acid-forming element, and the chromates are derived from the hypothetical **chromic acid**, H_2CrO_4 . This acid has not been obtained in the free state, as it breaks up into chromium trioxide and water when set free from its compounds, just as do carbonic and sulphurous acids. It is believed that these acids exist in aqueous solution, for when chromium trioxide is dissolved in water and the solution is neutralized by a base, a *chromate* is formed. The **chromates** in general resemble the sulphates; probably chromic acid is similar in structure to sulphuric acid, and should be represented by the formula H_2CrO_4 . It has been stated that sulphuric acid loses water and forms pyrosulphuric or disulphuric acid. In the same way, theoretically, chromic acid is converted into dichromic acid. Neither of these acids exists in the free state, but in all probability the relation between chromates and dichromates is the same as between sulphates and disulphates. By treating a chromate with an acid, a dichromate is obtained. Thus, if potassium chromate is treated with nitric acid, the following reaction takes place:



On the other hand, if a dichromate is treated with an alkali hydroxide, a chromate results. This may be illustrated by the equation:



62. Potassium Chromate.—Potassium chromate, K_2CrO_4 , is obtained by adding potassium hydroxide to the solution of the dichromate. It crystallizes in yellow rhombic crystals, is permanent in the air, has a cooling taste, and an alkaline reaction. It dissolves very easily in water and is therefore difficult to purify; for this reason it is usually converted into the dichromate, which is readily purified.

63. Potassium Dichromate.—Potassium dichromate, $K_2Cr_2O_7$, is prepared from chromite. The chromite is roasted

and is then ground and mixed with potassium carbonate and lime and heated. Calcium and potassium chromates are formed, and these are dissolved in water. Potassium sulphate is added to the solution, when calcium sulphate is precipitated and all the chromium is converted into potassium chromate. The solution is then treated with the proper amount of sulphuric acid, thus converting the chromate into the dichromate. As it dissolves in 10 parts of water at ordinary temperature, and is much more soluble in hot water, it crystallizes, on cooling, in large red plates belonging to the triclinic system. As the dichromate crystallizes well, it is easily purified by recrystallization. The chromate and dichromate may be regarded as the starting point for the preparation of the other compounds of chromium. When heated, the dichromate fuses without decomposing, but at a higher temperature it breaks up into potassium chromate, chromic oxide, and oxygen. When heated with sulphuric acid, the potassium and chromium unite with the acid, forming chrome alum. Water is also evolved, and all the oxygen not used in the formation of these is set free.

Potassium dichromate is largely used as an oxidizing agent. It is also used in dyeing, and to a certain extent in photography, and as the starting point for the preparation of nearly all the other chromium compounds.

64. Sodium Chromate.—Sodium chromate, Na_2CrO_4 , is obtained just as is potassium chromate; and by treating it with an acid, *sodium dichromate*, $\text{Na}_2\text{Cr}_2\text{O}_7$, is obtained. These compounds closely resemble the corresponding potassium salts, and are now used extensively in place of the more expensive potassium compounds.

65. Barium Chromate.—Barium chromate, BaCrO_4 , is obtained as a yellow precipitate when a soluble chromate is added to the solution of a barium salt. It is insoluble in water and in acetic acid, but dissolves in nitric and hydrochloric acids. It is used somewhat as a pigment under the name of *lemon yellow*.

66. Lead Chromate.—Lead chromate, PbCrO_4 , occurs in nature as crocoisite. It may be prepared by adding a solu-

ble chromate or dichromate to the solution of a lead salt, when the chromate separates as a yellow precipitate that is used as a pigment under the name of *chrome yellow*. When treated with a small quantity of a dilute solution of a hydroxide, it turns red, owing to the formation of basic lead chromate, Pb_2OCrO_4 , known as *chrome red*. This is used in dyeing, by dyeing the substance in chrome yellow and then dipping it in a bath of lime water, when the chrome yellow is changed to chrome red, and the substance is consequently dyed red.

67. Silver Chromate.—Silver chromate, Ag_2CrO_4 , is formed as a brick-red precipitate when a solution of silver nitrate is treated with a solution of potassium chromate. The dichromate is obtained when potassium dichromate is added to a slightly acid solution of silver nitrate. It forms small scarlet triclinic crystals.

MOLYBDENUM, TUNGSTEN, URANIUM, AND MANGANESE

MOLYBDENUM

Symbol Mo. *Atomic weight* 96. *Molecular weight* 96. *Valence* II, III, IV, and VI.

68. Occurrence and Properties.—Molybdenum occurs principally as sulphide, or *molybdenite*, MoS_2 , as lead molybdate, or *wulfenite*, $PbMoO_4$, and frequently as *molybdenum ochre*, MoO_3 . It is prepared by reducing the oxides or chlorides of molybdenum by a current of hydrogen at a high temperature. It is a white, very hard, brittle metal, and is almost infusible. It has a specific gravity of 10.28 at $26^\circ C.$, and oxidizes, when heated in the air, to molybdenum trioxide. It forms four oxides: MoO , Mo_2O_3 , MoO_2 , and MoO_3 .

COMPOUNDS OF MOLYBDENUM

69. Oxides.—*Molybdenum trioxide*, MoO_3 , frequently called *molybdic acid*, is obtained by roasting at a moderate temperature the natural molybdenite, MoS_2 ; the resulting oxide is dissolved in ammonia and the solution filtered. On evaporation and cooling, crystals of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, are obtained, which yield molybdenum trioxide when strongly heated in the air. Molybdenum trioxide is a white, fusible, volatile powder.

Molybdic oxide, Mo_2O_3 , is formed as a black precipitate when a solution of the trioxide is treated with a reducing agent, such as sodium amalgam.

Molybdenum dioxide, MoO_2 , a dark-blue compound, obtained by gently heating molybdenum or molybdic oxide in air.

Molybdenum monoxide, MoO , is obtained as a black precipitate, by treating a solution of molybdenum dichloride with a hot solution of potassium hydroxide.

70. Molybdic Acid.—It has been found that molybdenum trioxide is sparingly soluble in water, giving an acid solution. If this solution is neutralized by bases, molybdates are formed that are similar to the chromates in composition. When the ammonium salt thus obtained is treated with dilute nitric acid it is decomposed, and **molybdic acid**, $H_2MoO_4 \cdot H_2O$, crystallizes out of the solution. A number of salts are derived from this acid; but as the acid has a great tendency to combine with itself, most of the salts are derived from polymolybdic acids. Molybdic acid also unites with other acids, forming complicated acids that unite with bases forming complex salts. The best known of these acids is *phosphomolybdic acid*, a combination of phosphoric and molybdic acids. When phosphoric acid or a soluble phosphate is added to a solution of ammonium molybdate in an excess of nitric acid, a yellow precipitate of *ammonium phosphomolybdate* separates; this is a salt of phosphomolybdic acid, having the formula



(U. S. P., page 539)

TUNGSTEN

Symbol W. Atomic weight 184. Molecular weight 184. Valence II, IV, and VI.

71. Occurrence and Preparation.—Tungsten occurs in nature in a few minerals. Its symbol, *W*, is derived from the mineral *wolframite*, which is tungstate of iron and manganese, and from which it was first obtained; it occurs in *scheelite*, which is calcium tungstate; in *stolzite*, which is lead tungstate; etc. Metallic tungsten is obtained by reducing tungsten trioxide, WO_3 , with hydrogen or aluminum powder as an iron-gray metal of specific gravity 18.77. It is extremely hard, melts at $3,267^\circ \text{C.}$, and is unaffected by either hydrochloric or sulphuric acid, though it is converted into tungstic acid by the action of nitric acid. When dissolved in about ten times its own weight of fused steel, tungsten forms an extremely hard alloy, known as *tungsten steel*, that is used in the manufacture of machinists' tools. One of the most peculiar properties of tungsten is its ability to increase the magnetic power of the steel with which it is alloyed. A horseshoe magnet of ordinary steel, weighing 2 pounds, for instance, is generally considered of very good quality if it bears seven times its own weight, but a similar magnet made of an alloy of steel and tungsten is able to bear nearly twenty times its own weight.

COMPOUNDS OF TUNGSTEN

72. Tungsten Trioxide.—Tungsten trioxide, WO_3 , is obtained by decomposing metallic tungstates with nitric acid, and heating the tungstic acid thus precipitated. It is a canary-yellow powder, becoming orange when heated and yellow again when cooled.

73. Tungstic Acid.—When tungsten trioxide is fused with the proper amount of potassium carbonate, or solutions of these substances are mixed in the proper proportions, *potassium tungstate*, K_2WO_4 , is formed; if a solution of this compound is treated with a strong acid, **tungstic acid** is

precipitated. If the solution is hot, the acid has the composition H_2WO_4 ; but if at ordinary temperature, the precipitate has the composition $H_2WO_4 \cdot H_2O$, corresponding to molybdic acid. Like molybdic acid, tungstic acid has a tendency to unite with itself, forming polytungstic acids, and with other acids, forming complex acids. These combine with bases, forming very complicated compounds.

URANIUM

Symbol U. Atomic weight 238.2. Molecular weight 238.2. Valence II, IV, and VI.

74. Occurrence and Preparation.—The most important sources of uranium are the minerals *pitchblende*, or *uraninite*, and *carnotite*; deposits of the former are found in North Carolina, Cornwall, England, and German East Africa, while the latter occurs in Colorado.

The pure metal may be prepared by strongly heating a mixture of the tetrachloride, UCl_4 , with metallic sodium covered with sodium and potassium chlorides. The experiment is carried out in a crucible enclosed in a second crucible containing charcoal, so as to insure the exclusion of air. It can be prepared also by heating the oxide, *pitchblende*, U_3O_8 , in an electric furnace with about one-tenth its weight of charcoal.

75. Properties.—Uranium is a white metal, capable of taking a high polish, and somewhat softer than steel, and is malleable. Its specific gravity is 18.7. It melts at 800° C. and is permanent in the air. It combines directly with fluorine at ordinary temperatures; with chlorine, bromine, iodine, sulphur, and oxygen at a moderate heat; and with nitrogen at a bright-red heat. It decomposes water slowly at ordinary temperatures, and very rapidly at about 100° C. With carbon at high temperatures, it forms a carbide, U_2C_3 , that acts on water, forming a mixture of gaseous, liquid, and solid hydrocarbons. The metal and its salts are radioactive; all its salts are powerful poisons.

COMPOUNDS OF URANIUM

76. Oxides.—As stated, uranium occurs in nature in the form of the **oxide**, U_3O_8 , which is also the final product of the oxidation of uranium in the air. When this oxide is treated with nitric acid, uranyl nitrate is formed, and when this is heated, uranium trioxide is formed. The dioxide is formed by reducing the trioxide by means of hydrogen. When either of these oxides is ignited in the air, U_3O_8 results. The *tetroxide*, UO_4 , is obtained as a light-yellow precipitate by adding hydrogen peroxide to a uranyl salt.

77. Chlorides.—*Uranium tetrachloride*, UCl_4 , is formed when chlorine acts on finely divided uranium, but this is usually accompanied by some pentachloride. By reducing this with hydrogen, the *trichloride*, UCl_3 , is obtained; and by heating the tetrachloride for some time in chlorine it is partially converted into the pentachloride. The *tetrachloride*, UCl_4 , is the most stable of the chlorides.

78. Uranous and Uranyl Salts.—The few uranous salts are derived from tetravalent uranium, 1 atom replacing 4 of hydrogen, as shown by the sulphate, $U(SO_4)_2$. In the uranyl compounds, the group UO_2 acts like a bivalent metal. The salts formed may be illustrated by the sulphate, UO_2SO_4 , and the nitrate, $UO_2(NO_3)_2$. These salts, it is evident, are derived from the hydroxide, $UO_2(OH)_2$, which acts as a base in the presence of acids.

79. Uranates.—It has just been shown that in the presence of acids, the hydroxide, $UO_2(OH)_2$, acts as a base. In the presence of some of the stronger bases it also acts as an acid. When a uranyl salt is acted on by an alkali hydroxide, a precipitate is formed having the composition $M_2U_2O_7$, and is therefore derived from an acid, $H_2U_2O_7$, which is analogous to dichromic acid, and is known as diuranic acid. One of the most important derivatives of this acid is *sodium diuranate*, $Na_2U_2O_7$, a yellow powder that is manufactured in large quantities and used in coloring glass. (U. S. P., page 483.)

RADIOACTIVE ELEMENTS

80. It was discovered by Becquerel that uraninite, or pitchblende, emitted a peculiar kind of rays which move in a straight line, act on a photographic plate, and cannot be reflected or refracted. Gases become electrical conductors when these rays are passed through them. For a while it was thought that this radioactivity was due solely to the uranium present; but M. and Mme. Curie have proved that the radioactivity is largely caused by three hitherto unknown elements which they called *radium*, *polonium*, and *actinium*. The amounts of these elements present were very minute, and in order to separate them from the residues left after extracting the uranium, these were subjected to numerous chemical operations and the success in concentration judged by measuring the conductivity of an air layer exposed to the rays. It will be observed that for the discovery of these elements an entirely new method of testing was introduced.

81. Radium is the most thoroughly investigated of these elements and has been obtained nearly pure as chloride. It has an atomic weight, according to Mme. Curie, of 226. It accompanies the barium chloride extracted from uraninite and is separated from it by fractional crystallization, the radium chloride being less soluble than barium chloride. About 1 gramme of radium chloride was separated in this manner from 80 tons of ore. The process is simplified by recrystallizing with the bromides instead of the chlorides. It has a characteristic spectrum resembling that of the alkaline earths. Radium compounds give light in the dark; when they are very concentrated they transform oxygen into ozone and have an odor like sodium hypochlorite. Under the influence of the rays emitted, glass assumes a brown color and potassium and sodium chlorides turn blue.

Polonium is found with bismuth extracted from uraninite; its chemical properties are similar to bismuth. The sulphide is more volatile in vacuo than bismuth sulphide, which property is taken advantage of in separating it.

MANGANESE

Symbol Mn. Atomic weight 54.93. Molecular weight 54.93. Valence II, III, IV, VI, VII.

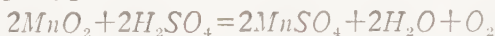
82. History and Occurrence.—Manganese was discovered by Scheele and Bergmann in 1774, in a mineral known as *braunstein*. Owing to its being confounded with magnetic iron, this mineral had received the Latin name of this substance, that is, *magnesia nigra*; whence the name magnesium first was assigned to the new metal. This name was afterwards changed to manganese, to distinguish it from true magnesium obtained from the *magnesia alba*. It is found chiefly as *pyrolusite*, MnO_2 , *braunite*, Mn_2O_3 , and *rhodochrosite*, $MnCO_3$. Manganese sulphide, arsenide, and silicate are also known as minerals. The metal itself has not been applied to any very useful purpose in the arts, but forms some useful alloys.

Manganese is best prepared by reducing MnO_2 by means of aluminum powder. It is a grayish-white, hard, brittle metal, having a specific gravity of 7.42, is feebly magnetic, fuses at $1,260^\circ$ C., and volatilizes at the temperature of the electric furnace. It will take a high polish, but oxidizes readily in the air unless it contains iron. It decomposes water at but little above the ordinary temperature, is easily soluble in all dilute acids, and combines with carbon and nitrogen at a high temperature.

COMPOUNDS OF MANGANESE

83. Manganese Dioxide.—Manganese dioxide, or *peroxide*, MnO_2 , the chief compound and most important one of manganese, occurs in nature as *pyrolusite* in amorphous masses, in crystalline masses, or in steel-gray, rhombic crystals. It has a metallic luster, a black streak, and is opaque and brittle. The mineral contains from 70 to 90 per cent. of manganese dioxide, which has a specific gravity of 5.026. Manganese dioxide is also found in the hydrated state as *wad*. *Pyrolusite* is frequently known as the *black oxide of manganese*. It is largely used in the manufacture of steel,

although frequently replaced by alloys of iron and manganese such as *spiegeleisen* and *ferromanganese*, the manufacture of bleaching powder, in the making of glass, and as a source of oxygen. Manganese dioxide does not combine readily with acids, although hydrochloric acid dissolves it, giving a brown solution. If this solution is heated chlorine is evolved and the pink manganese chloride is obtained. Nitric acid has almost no action on the dioxide, but strong sulphuric acid dissolves it, evolving oxygen, thus:



Dilute sulphuric acid in the presence of some readily oxidizable substance, such as oxalic acid or ferrous sulphate, produces the same effect.

Heating with hydrogen does not reduce the oxides of manganese to metallic manganese but forms manganous oxide, MnO . (U. S. P., page 266.)

84. Manganous Oxide.—Manganous oxide, MnO , or *manganese monoxide*, is obtained by the preceding method, or by fusing a mixture of anhydrous manganese chloride, sodium carbonate, and ammonium chloride. It forms a green powder, which, when heated in hydrogen, crystallizes in emerald-green octahedra having an adamantine luster and a specific gravity of 5.1. It is soluble in acids, forming the manganous salts, absorbs oxygen from the air, and fuses at a white heat without loss of oxygen. It is found in nature as the mineral *manganosite*.

85. Manganic Oxide.—Manganic oxide, Mn_2O_3 , or *manganese sesquioxide*, occurs as the mineral *braunite* in octahedral crystals. It closely resembles the dioxide, has a brownish-black color, a semi-metallic luster, and a specific gravity of 4.8. It is soluble in strong sulphuric acid, is feebly basic, and may be obtained by heating any of the oxides of manganese to redness in a current of oxygen. Added to melted glass it imparts a purple color to it.

86. Red Oxide of Manganese.—Red oxide of manganese, Mn_3O_4 , *trimanganese tetroxide*, is found crystallized in

tetragonal pyramids as the mineral *hausmannite*. It is the most stable of the oxides and is formed when any of the others is heated in the air. It is a brown or reddish-brown powder having a specific gravity of 4.7, and resembles the corresponding lead oxide. It is probably a manganous manganic oxide having the formula $MnO \cdot Mn_2O_3$.

87. Manganese Heptoxide.—Manganese heptoxide, Mn_2O_7 , also known as *permanganic anhydride*, is a red, oily liquid prepared by the gradual addition of strong sulphuric acid to potassium permanganate, thus:



It is an extremely unstable compound, decomposing, at ordinary temperatures, with the evolution of oxygen, the decomposition being also accompanied by the emission of the violet fumes of the heptoxide. It absorbs moisture from the air, and is a powerful oxidizing agent, setting fire to most combustible bodies.

88. Manganous Hydroxide.—Manganous hydroxide, $Mn(OH)_2$, forms as a white precipitate when an alkali is added to a solution of a manganous salt out of contact with the air. It must be dried in a current of hydrogen, as it speedily oxidizes to Mn_2O_3 when exposed to the air. It occurs in nature as the mineral *pyrochroite*.

89. Manganic Hydroxide.—Manganic hydroxide, $MnO(OH)$, occurs in nature in steel-gray crystals as the mineral *manganite*. It gives a brown streak on unglazed porcelain and has a specific gravity of 4.3. It is formed when manganous hydroxide is allowed to stand in the air for a short time. Dilute nitric acid dissolves part of it, forming manganous nitrate, the remainder being converted into the dioxide.

90. Manganous Chloride.—Manganous chloride, $MnCl_2$, is formed by dissolving any of the oxides or hydroxides, or the carbonate of manganese in hydrochloric acid, with the aid of heat. It is obtained in large quantities as a by-product in the preparation of chlorine for use in the manufacture of

bleaching powder. When a solution containing the chloride is sufficiently concentrated, the chloride separates in pink crystals having the composition $MnCl_2 \cdot 4H_2O$. When heated, these crystals fuse to an oily liquid and in moist air at this temperature are decomposed into the oxide and hydrochloric acid.

If manganic hydroxide is dissolved in cold hydrochloric acid, a brown solution is obtained that is believed to contain manganese trichloride, $MnCl_3$. Similarly, if the dioxide is dissolved in cold hydrochloric acid, a brown solution is obtained that is thought to be manganese tetrachloride, $MnCl_4$. Neither of these compounds have been isolated, and if allowed to stand they gradually lose chlorine and become pink when the content of chlorine is reduced to that indicated by the formula $MnCl_2$. If heat is applied, this change takes place rapidly.

91. Manganous Sulphate.—Manganous sulphate, $MnSO_4$, is prepared by dissolving manganous carbonate, $MnCO_3$, in sulphuric acid, or by heating a paste of manganese dioxide and sulphuric acid to redness and leaching with water. The properly concentrated rose-colored solution deposits, between 0° and 6° C., oblique rhombic prisms, isomorphous with green vitriol and containing 7 molecules of water. Between 7° and 20° C., manganous sulphate crystallizes with 5 molecules of water, like cupric sulphate, with which it is then isomorphous. Between 20° and 30° C., it is deposited in oblique rhombic prisms that then contain only 4 molecules of water. All of these crystals are pink-colored, and their color is deeper the more water of crystallization they contain; all are extremely soluble in water. (U. S. P., page 537.)

92. Manganous Sulphide.—Manganous sulphide, MnS , or *manganese monosulphide*, occurs in nature as the mineral *alabandite*, in steel-gray crystalline masses having a green streak. It is prepared by heating one of the oxides of manganese, or manganese carbonate in a current of hydrogen sulphide. It is obtained in this way as a dark powder, but when heated to a high temperature it melts and forms a steel-gray crystalline mass. Alkaline sulphides precipitate manganous sulphide from solutions of manganous salts as a flesh-colored

precipitate that turns brown on exposure to the air. When the flesh-colored precipitate is boiled with an excess of alkaline sulphide it changes into a green crystalline mass. Manganous sulphide unites with the alkaline sulphides, forming salts, and is soluble in hydrochloric acid.

The *disulphide*, MnS_2 , occurs as *hauerite*, has a metallic luster, and a reddish-brown color.

93. Manganic Acid.—Manganic acid, H_2MnO_4 , has not been obtained, but salts of the acid, *manganates*, isomorphous with the sulphates and chromates, are known. The manganates are green in color, and their solutions are unstable except in the presence of considerable free alkali. Treated with carbon dioxide or made slightly acid, they are converted into the corresponding permanganate. In an alkaline solution the manganates are powerful oxidizing agents.

94. Potassium Manganate.—Potassium manganate, K_2MnO_4 , is prepared by fusing a mixture of manganese dioxide and caustic potash, thus:



In the presence of an oxidizing agent the sesquioxide is converted into the manganate.

Potassium manganate is a green-colored mass soluble in water.

95. Sodium Manganate.—Sodium manganate, Na_2MnO_4 , is formed in the same manner as the potassium salt, and crystallizes with 10 molecules of water, the formula being $Na_2MnO_4 \cdot 10H_2O$. This solution is used as a deodorizer and is used for disinfecting purposes under the name of *Condy's green disinfecting fluid*.

96. Permanganic Acid.—Permanganic acid, $HMnO_4$, is prepared by the addition of sulphuric acid to barium permanganate, or by the electrolysis of potassium permanganate. It is a deep-red liquid having a bitter metallic taste, and readily decomposes under the action of light or heat.

97. Potassium Permanganate.—Potassium permanganate, $KMnO_4$, is prepared by heating to dull redness a

mixture of manganese dioxide, potassium hydroxide, and potassium chlorate. The dark-green mass obtained is leached with boiling water, and the solution is filtered and allowed to crystallize. The crystals are dark violet, almost black prisms, with a steel-blue metallic luster, have a sweet taste, with an astringent after taste. They have a specific gravity of 2.7, are soluble in 16 parts of water, forming a deep purple-colored solution, and decomposes at 240° C.

Potassium permanganate is a powerful oxidizing agent, its solution being bleached by substances such as ferrous salts, etc., these substances being raised to a higher valence in the process. Thus, the action of ferrous sulphate on potassium permanganate breaks the permanganate up into potassium sulphate and manganese sulphate, while the ferrous sulphate is oxidized to ferric sulphate, according to the following equation:



Organic substances, especially the offensive emanations from putrescent organic matter, are readily oxidized by potassium permanganate. It is extensively used under the name of *Condy's red disinfecting fluid*. (U. S. P., pages 342, 545, and 568.)

98. Sodium Permanganate.—Sodium permanganate, $NaMnO_4$, is prepared in a similar manner to the potassium salt. It is distinguished from the latter by its being deliquescent. Being cheaper than potassium permanganate, it is frequently used in place of the more expensive salt.

IRON, COBALT, AND NICKEL

IRON

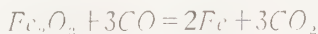
Symbol Fe. Atomic weight 55.84. Molecular weight 55.84. Valence II and III.

99. History and Occurrence.—Iron has been known from the earliest historic times and is one of the most useful metals and at the same time one of the most widely and abundantly diffused in nature. As found on the earth's surface, native iron generally contains nickel and is of meteoric origin. It occurs in plants and vegetables, and is an essential constituent of the animal body. Among the more important minerals in which it is found may be mentioned *hematite*, Fe_2O_3 ; *magnetite*, Fe_3O_4 ; *limonite*, or *brown hematite*, $2Fe_2O_3 \cdot 3H_2O$, or $Fe_4O_3(OH)_6$; *siderite*, $FeCO_3$; *pyrite*, FeS_2 ; and *pyrrhotite*, Fe_7S_8 . It also occurs in many silicates, to which it usually imparts a red color. Of these, hematite, magnetite, limonite, and siderite are used as ores.

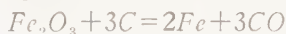
These ores are frequently associated with extraneous minerals that injure the quality of the iron. It is worthy of notice that scarcely one of these ores is entirely free from sulphur and phosphorus, substances that not only have a serious effect on the quality of the iron extracted from those ores, but also, by their presence in the iron, increase the difficulty of obtaining it in a marketable condition.

100. Preparation.—In the arts, iron is obtained on a large scale, either from the natural oxide, carbonate, or hydrated oxide. The ore, fuel, and limestone are placed in a *blast furnace*, which is from 40 to 100 feet high, and is shaped on the inside like a double cone. A powerful blast of hot air enters at the bottom, and the combustible matter, at the high

temperature thus produced, removes the oxygen from the ore, reducing it to the metallic state. The principal reducing agent is carbon monoxide, in which case the reaction may be written:



But the reduction is also partially accomplished by means of the carbon of the fuel, in which case the reaction may be represented by the equation:



101. The limestone unites with the silica and other impurities present, forming a fusible silicate that collects above the melted iron and is drawn off as *cinder* or *slag*. After the iron is reduced to the metallic state, it takes up more carbon, becomes fusible, melts, and runs down to the bottom of the furnace, which is called the *crucible*, or *hearth*. When enough has collected, it is tapped by drilling through the clay plug that closes the opening and the melted iron runs down a suitable channel into molds made in the sand for its reception. The manufacture of cast iron in the blast furnace is a continuous operation; the materials are constantly added above, and the cinder and melted iron are drawn off from below generally about five times a day, until the furnace needs repairs, or until other reasons put a temporary stop to further manufacturing. The frequency with which the iron, as well as the cinder, is drawn off varies in different places and under different conditions; it depends largely on the rapidity with which the iron is being produced. The iron thus obtained is known in the market as *cast*, or *pig*, *iron*.

Pure iron may be prepared from the best commercial varieties, piano wire for instance, by fusing them in a clay crucible with pure iron oxide, beneath a layer of glass to keep out the air.

102. Properties.—Pure iron is brilliant silver-white in color, softer than wrought iron, capable of receiving a high polish, strongly magnetic, of specific gravity 7.8, and crystallizes in the regular system. Iron is also prepared for pharmaceutical purposes by reducing its oxide by hydrogen at a red

heat. It is then obtained as a black powder, which burns when heated in the air. In its purest commercial form, iron has a greater tenacity than any other metal, except nickel and cobalt. Its ductility is also very great, and when heated it may be rolled into sheets scarcely thicker than paper. At a full red heat it becomes pasty like wax, and may then be welded. It melts at a temperature of about $1,530^{\circ}$ C., whereas cast iron melts at $1,100^{\circ}$ to $1,300^{\circ}$ C., wrought iron $1,800^{\circ}$ to $2,200^{\circ}$ C., and steel from $1,300^{\circ}$ to $1,600^{\circ}$ C. (U. S. P., pages 172 and 536.)

103. Steel.—Steel, according to the American usage of the term, is iron that has been treated by one of several processes. The products included under this name contain from less than .1 to more than 1.5 per cent. of carbon, and possess nearly all the chemical and physical properties, except those peculiar to cast iron, that belong to the commercial forms of this metal. Several methods may be employed for producing steel, but only two of the most important, from a commercial viewpoint, will be considered here, namely: (a) The Bessemer process, and (b) the open-hearth process.

(a) The *Bessemer process* derived its name from its inventor, Henry Bessemer. The molten pig iron is run into a large egg-shaped vessel, called the *converter*. This is made of iron plates bolted together and lined with a siliceous rock, called *ganister*. The bottom, which is interchangeable, contains a number of small openings, or *tuyères*, about $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter, through which air is blown at a pressure of about 25 pounds per square inch. The converter is turned into a horizontal position to receive the charge of from 5 to 20 tons, which has previously been melted in a cupola, and it is then replaced in a vertical position, while at the same time a moderate blast of air is sent through the tuyères.

This blast is employed for the purpose of burning the impurities from the iron and, incidentally, it prevents the molten iron from running into the tuyères. The silicon, manganese, carbon, and a portion of the iron burn in the stream of air, producing a very high temperature, which serves to keep the

iron in a molten condition. The carbon is converted into carbon monoxide, which burns with a long flame at the mouth of the converter and is usually accompanied by a stream of sparks from the combustion of the iron. The blow is continued until the flame of carbon monoxide disappears. If continued longer the combustion proceeds at the expense of the iron. The blast pressure is then lowered and the necessary amount of spiegeleisen or ferromanganese added and the blast turned on again for a few minutes, after which the molten steel is run into ingot molds by tilting the converter. This process, as described, requires an iron practically free from sulphur and phosphorus. If, however, the converter is lined with a basic material, as done by Gilchrist and Thomas, using a calcined dolomite, pig iron containing varying amounts of phosphorus can be used.

(b) In the *open-hearth process* a reverberatory furnace built over regenerating flues is used. These flues are heated by the waste gases from the furnace and in turn heat the gas and air passing to the hearth of the furnace.

The charge of pig iron, scrap iron, steel, and limestone is melted on the hearth of the furnace by a flame of carbon monoxide raised to a high temperature by the regenerators. When the charge has melted, iron ore, generally hematite, and some limestone are added. A violent boiling now ensues and slag is formed by the silica, obtained by the oxidation of the silicon present, combining with the ferrous oxide of the ore. The carbon is next removed by oxidizing it to carbon monoxide, and the phosphorus goes into the slag. A test piece of steel is withdrawn and the end of the process determined by the fracture and analysis of this test. When the process is complete, the steel is run into a ladle, and ferromanganese is added if required to deoxidize and recarbonize, and then the steel is run into ingots.

Liquid metal direct from the blast furnaces is generally used in place of pig iron.

104. Properties of Steel.—As steel is a term applied to a variety of material, produced by various processes, and dif-

fering in chemical composition, its properties cannot be definitely stated, but differ with the different varieties. The so-called *mild steel*, which contains a low percentage of carbon, is relatively soft and malleable and probably cannot be hardened by any physical treatment. On the other hand, steel that contains more carbon, if heated to a rather high temperature and suddenly cooled, or "quenched," by dipping it in cold water, becomes very hard. A steel containing a high percentage of carbon becomes much harder when treated in this way than one containing a smaller quantity of this element, and those samples containing but mere traces of carbon, as stated before, cannot be hardened to any considerable extent by this process. It thus appears that the property of hardening when suddenly cooled from a high temperature depends largely, if not entirely, on the carbon content of the steel. Careful study and examination of steel under varying conditions have led to the belief that the phenomena attending the hardening and softening of steel by changes of temperature are due to the forms assumed by the carbon under varying conditions.

OXIDES OF IRON

105. Three oxides of iron are known, namely: *ferrous oxide*, FeO ; *ferric oxide*, Fe_2O_3 ; *ferrous-ferric oxide*, Fe_3O_4 .

106. Ferrous Oxide and Ferrous Hydroxide.—Ferrous oxide, FeO , may be obtained as a black powder by igniting ferrous oxalate in a closed vessel. Ferrous hydroxide, $Fe(OH)_2$, is formed as a white precipitate when an alkaline hydroxide is added to the solution of a ferrous salt. White flocks are thus produced, which, dried away from the air, have a slightly greenish tint, but which, on exposure, take fire and burn to ferric oxide. Ferrous oxide has a strong reducing action.

107. Ferric Oxide.—Ferric oxide, Fe_2O_3 , which occurs abundantly in nature, is called *hematite*, and is one of the most important of the iron ores. Artificially it may be prepared by igniting the hydroxide or by calcining ferrous sulphate. This

salt first loses its water, and then at red heat decomposes into sulphur trioxide, sulphur dioxide, and ferric oxide:



A red powder is thus obtained, which is known in commerce under the name of *colcothar*, *rouge*, and *Venetian red*, and is used for polishing metals, glass, etc. Its specific gravity is 5.2. It is reduced to the metallic state when heated in hydrogen.

108. Ferric Hydroxide.—Ferric hydroxide, $Fe(OH)_3$, is prepared by adding ammonium hydroxide to the solution of a ferric salt, when it separates as a brownish-red precipitate, which may be washed and dried at a moderate temperature without decomposing. If, however, it is heated to $100^\circ C.$, or if the solution containing it is boiled for some time, it gradually loses water, forming the hydroxides $FeOOH$, $Fe_2O(OH)_4$, etc. When strongly ignited, these give up more water and are converted into ferric oxide. The hydroxide $FeOOH$ corresponds to the compounds $AlOOH$ and $CrOOH$, and is believed to form some salts.

109. Ferrous-Ferric Oxide.—Ferrous-ferric oxide, Fe_3O_4 , is found in nature as the mineral *magnetite*, and is believed to be a combination of the oxides of iron, FeO and Fe_2O_3 .

Ferrous-ferric oxide is formed when iron is burned in oxygen, or when steam is passed over red-hot iron.

The very stable character of Fe_3O_4 has permitted its application for protecting iron from rust. When superheated steam is passed over the red-hot metal, a very dense, strongly adhering film of Fe_3O_4 is produced, which effectually protects the metal (*Barff's process*). A similar coating is produced by the action of a mixture of air and carbon dioxide (*Bower's process*).

110. Ferric Acid.—Ferric acid, H_2FeO_4 , while not known in the free state, forms ferrates, some of which are fairly well known. A solution of the potassium salt is formed when iron filings and potassium nitrate are strongly ignited,

and the fused mass is extracted with water. The solution has a fine purple color. It can be prepared also by passing chlorine through a strong solution of caustic potash containing freshly precipitated ferric hydroxide in suspension. Potassium ferrate forms a black precipitate, insoluble in alkaline solutions, but soluble in water. It is very unstable. The solution decomposes on boiling with an evolution of oxygen, and precipitation of ferric hydroxide.

The ferrate of barium is prepared by adding barium chloride to a solution of either potassium or sodium ferrate. It is a dark-red powder, soluble in acetic acid, and fairly stable.

111. Ferrous Carbonate.—Ferrous carbonate, $FeCO_3$, occurs in nature as *siderite*, or *spathic iron ore*, in obtuse rhombohedrons, light grayish or yellowish in color, and of specific gravity 3.8. It is thrown down, on the addition of a soluble carbonate to a solution of a ferrous salt, as a white precipitate, rapidly passing into brown ferric hydroxide. It is soluble in water containing carbonic acid and is found in this state in nature in the waters of chalybeate springs. (U. S. P., pages 165, 267, and 324.)

SULPHIDES OF IRON

112. Iron Disulphide.—Iron disulphide, FeS_2 , being widely diffused, as *iron pyrites*, is the most important of the sulphides of iron. It occurs in nature in two distinct forms: one, brass-yellow and isometric, is known as *pyrite*; and the other, white or dull greenish-yellow and orthorhombic, is called *marcasite*. This latter variety can be altered much more readily than the other, and possesses a great tendency to attract oxygen from the air and become converted into *sulphate*. When heated in closed vessels, pyrite loses a part of its sulphur. Iron disulphide may be obtained artificially by heating iron with excess of sulphur to a temperature below redness, or by heating ferric oxide or hydroxide moderately in a stream of H_2S as long as it increases in weight.

113. Ferrous Sulphide.—Ferrous sulphide, FeS , is found in small quantities in many meteorites. It may be pro-

duced by the direct union of iron and sulphur, as when iron wire burns in sulphur vapor, or when the two substances are melted together in suitable proportions. It is a grayish-yellow solid with a metallic luster and crystalline structure, and is easily fusible. When finely divided, it is oxidized to ferrous sulphate on exposure to the air. With acids it evolves hydrogen-sulphide gas. It is precipitated from ferrous solutions by alkaline sulphides.

114. Ferric Sulphide.—Ferric sulphide, Fe_2S_3 , may be prepared by heating iron and sulphur mixed in the proper proportions. It is not commercially important, and is interesting, theoretically, principally because it is analogous to Fe_2O_3 . Just as the hydroxide, $FeOOH$, corresponding to the oxide Fe_2O_3 , forms salts, so does the hydrosulphide $FeSSH$.

CHLORIDES OF IRON

115. Ferrous Chloride.—When hydrochloric-acid gas is passed over iron filings heated to redness, ferrous chloride, $FeCl_2$, is obtained in white, shining, hexagonal scales that have a specific gravity of 2.5 and are deliquescent in moist air. It is soluble in 2 parts of water, and the solution, evaporated and cooled away from the air, deposits crystals having the composition $FeCl_2 \cdot 4H_2O$. When heated in the air to drive off the water, these crystals decompose. Ferrous chloride may be prepared in solution by dissolving iron in hydrochloric acid, away from air. If the solution containing hydrochloric acid is exposed to air, the chloride will be oxidized to ferric chloride; but if the solution does not contain hydrochloric acid, it breaks up into ferric chloride, which remains in solution, and a basic chloride, which separates as a precipitate. Ferrous chloride unites with the chlorides of the alkalies, forming double chlorides of the composition K_2FeCl_4 , Na_2FeCl_4 , etc.

116. Ferric Chloride.—Ferric chloride, $FeCl_3$, is most readily prepared in solution by dissolving iron in hydrochloric acid, and saturating the solution with chlorine. This solution, especially if dilute, is decomposed into hydrochloric acid and

an insoluble oxychloride when strongly heated. By treating the solution carefully, yellow crystals of $FeCl_3 \cdot 6H_2O$ may be obtained. These are decomposed into ferric oxide and hydrochloric acid if heated to drive off the water. The anhydrous chloride is obtained by heating iron in an atmosphere of chlorine. (U. S. P., page 166.)

SULPHATES OF IRON

117. Ferrous Sulphate.—Ferrous sulphate, $FeSO_4$, long known under the names of *copperas* and *green vitriol*, is prepared by dissolving iron wire in dilute sulphuric acid. It is obtained as a by-product in the manufacture of copper sulphate, and by the decomposition of pyrite or marcasite.

Ferrous sulphate crystallizes in fine, green, monoclinic crystals, having the composition $FeSO_4 \cdot 7H_2O$ and a specific gravity of 1.9.

Ferrous sulphate dissolves readily in water and forms a pale-green solution. If this solution is heated, or upon long standing, it decomposes, forming a muddy solution, due to the oxidation of the sulphate and the formation of a basic sulphate. Ferrous sulphate readily absorbs oxygen and, hence, is frequently used as a reducing agent. In this capacity it is frequently used to precipitate gold in the metallic state from its solutions. Its principal use, however, is for the preparation of iron mordants for the dyeing industries, inks, Prussian blue, tanning, etc. (U. S. P., page 244.)

118. Ferric Sulphate.—Ferric sulphate, $Fe_2(SO_4)_3$, is obtained by treating a solution of ferrous sulphate, containing sulphuric acid, with an oxidizing agent, or by dissolving ferric hydroxide in sulphuric acid, and evaporating the solution. It is a slightly yellowish mass that dissolves completely, though rather slowly, in water. The solution is yellow-brown, and has an acid reaction. When concentrated by evaporation, it deposits a deliquescent, yellowish, crystalline mass of hydrated ferric sulphate.

Ferric sulphate unites with sulphates of the alkalis, forming double sulphates that are analogous to alum, and are

known as *iron alums*. The potassium salt has the composition $KFe(SO_4)_2 \cdot 12H_2O$.

119. Iron Phosphates.—*Ferrous phosphate*, $Fe_3(PO_4)_2$, occurs in nature with 8 molecules of water of crystallization, as the mineral *vivianite*. It may be precipitated from a ferrous solution by adding sodium phosphate.

Ferric phosphate, $FePO_4$, separates as a precipitate when sodium phosphate is added to a ferric solution. (U. S. P., page 169.)

NOTE.—Additional information on preparations containing iron is found in the U. S. P., pages 165, 166, 167, 168, 325, 429, and 532.

COBALT

Symbol Co. Atomic weight 58.97. Molecular weight 58.97. Valence II and III.

120. History and Occurrence.—The property, which certain cobalt compounds possess, of coloring glass blue was known to the ancients. The ores were long known to the German miners under the name of *cobalt*, a name derived from *kobold*, meaning a roguish spirit, who, as they supposed, offered them an ore rich in appearance but otherwise worthless. Brandt, in 1735, prepared the metal and his observations on its properties were confirmed by Bergman in 1780.

Cobalt does not occur free in nature except in meteoric iron. It usually occurs as *linnæite*, $(CoNiFe)_3S_4$; *speiss cobalt*, $CoNiFeAs_2$; *skutterudite*, $CoAs_3$; *smaltite*, $CoAs_2$; and *cobaltite*, $CoAs_2 \cdot CoS_2$.

121. Preparation and Properties.—Cobalt ores containing sulphur and arsenic are roasted and the roasted ores fused with lime or sand. The iron in the ore enters the slag, and the cobalt, in the form of *speiss*, that is, combined with arsenic, sinks. The speiss is dissolved in hydrochloric acid, when any arsenate of iron is precipitated by means of bleaching powder and calcium hydrate. The clear supernatant liquid is drawn off and the heavy metals, copper, bismuth, etc., precipi-

tated with hydrogen sulphide. Bleaching powder is added to the clear liquid remaining and the cobalt is precipitated as an oxide.

Metallic cobalt is prepared by igniting the oxide or the chloride in a current of hydrogen; by the electrolysis of the chloride; or by ignition of the chloride with sodium or potassium. It can be prepared also by heating the oxalate under powdered glass.

Cobalt is a silver-white metal, slightly tinged with red. It is harder than either iron or nickel, is malleable, and very ductile, and is magnetic. It melts at $1,478^{\circ}$ C., has a granular fracture and a specific gravity of 8.7. The compact metal does not change at the ordinary temperature, but the powder oxidizes very readily in the air. It is only slowly soluble in sulphuric and hydrochloric acids, evolving hydrogen, but is readily soluble in nitric acid.

COMPOUNDS OF COBALT

122. Cobalt forms three oxides: *cobaltous oxide*, CoO ; *cobaltic oxide*, Co_2O_3 ; and *cobaltous-cobaltic oxide*, Co_3O_4 .

123. Cobaltous Oxide.—Cobaltous oxide, CoO , is obtained when one of the higher oxides is heated in a current of hydrogen or of carbon dioxide. It is prepared also by heating cobaltous hydroxide in the absence of air. It is a decidedly basic oxide, is a light-brown powder unaffected by the air at ordinary temperatures, and dissolves in acids, forming cobaltous salts. Heated in the air, it forms cobaltous-cobaltic oxide.

124. Cobaltic Oxide.—Cobaltic oxide, Co_2O_3 , is obtained as a black powder when the nitrate is gently heated. It acts as a feeble base and is soluble in acids, when it forms the cobaltic salts, which are unstable. When heated it yields the cobaltous-cobaltic oxide.

125. Cobaltous-Cobaltic Oxide.—Cobaltous-cobaltic oxide, Co_3O_4 , is formed when any of the oxides or the nitrate is ignited in the air. It is a black powder, is used for the preparation of cobalt products and for painting on porcelain. Boiled with hydrochloric acid, it forms cobaltous chloride and

evolves chlorine. It is analogous to Fe_3O_4 and is believed to be a combination of the oxides, CoO and Co_2O_3 .

126. Cobaltous Hydroxide.—Cobaltous hydroxide, $Co(OH)_2$, is the precipitate obtained when potassium hydroxide is added in excess to a boiling solution of a cobaltous salt. A blue precipitate of a basic salt is first obtained, and this, on continued boiling, becomes converted into the rose-red hydroxide. This readily absorbs oxygen from the air, changing to the brown cobaltic hydroxide. *Cobaltic hydroxide*, $Co(OH)_3$, is obtained as a brownish-black precipitate when an alkaline hypochlorite solution is added to a solution of a cobalt salt.

127. Cobaltous Nitrate.—Cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$, can be prepared by dissolving cobaltous oxide in nitric acid, as



It forms red, deliquescent crystals that are easily soluble in water and melt somewhat under $100^\circ C.$, changing from red to blue when the water of crystallization has been expelled. On further heating, it is converted into cobaltic oxide. It is largely used as a blowpipe reagent.

128. Potassium-Cobaltic Nitrite.—When a solution of cobaltous nitrate is acidified with acetic acid and a solution of potassium nitrite is added, a yellow precipitate of potassium-cobaltic nitrite, or *cobalt yellow*, $K_6Co_2(NO_2)_{12}$, is obtained. It forms a yellow microcrystalline powder slightly soluble in water.

129. Cobaltous Chloride.—Cobaltous chloride, $CoCl_2$, is prepared by heating the powdered metal in chlorine gas, or by dissolving one of the oxides or the carbonate in hydrochloric acid. It crystallizes in red prisms with 6 molecules of water. Heated to $120^\circ C.$, these crystals change to the blue of the anhydrous salt. A solution of cobaltous chloride forms the so-called *sympathetic ink*, for characters written with its pink solution are almost invisible until exposed to heat, when they become blue, and on exposure to the air gradually resume their original pink color. (U. S. P., page 530.)

130. Cobaltous Sulphide.—By adding ammonium sulphide to a solution of a cobalt salt, a black precipitate of cobaltous sulphide, CoS , is obtained. It differs from ferrous sulphide in being insoluble in dilute hydrochloric acid.

131. Cobaltous Sulphate.—Cobaltous sulphate, $CoSO_4 \cdot 7H_2O$, occurs native as the mineral *bieberite*. It is prepared by dissolving the oxides or the carbonate in sulphuric acid. It crystallizes in red prisms isomorphous with ferrous sulphate, is not affected by the air, is soluble in water, has a weak, astringent, metallic taste, and is insoluble in alcohol. It is used for the manufacture of cobalt salts, and in decorating porcelain. It does not acquire a blue color when dried, and can be submitted to a high temperature without undergoing decomposition.

132. Cobaltous Arsenate and Diarsenide.—Cobaltous arsenate, $Co_3(AsO_4)_2$, occurs as *cobalt bloom* in violet needles containing 8 molecules of water of crystallization. It is soluble in dilute mineral acids. The diarsenide, $CoAs_2$, occurs as *smaltite*, or *speiss cobalt*, associated with iron and nickel.

NICKEL

Symbol Ni. Atomic weight 58.68. Molecular weight 58.68. Valence II and III.

133. History and Occurrence.—Nickel was discovered by Cronstedt, in 1751, in a copper-colored mineral, to which, having failed in attempting to extract copper from it, the miners had applied in derision the name *kupfernickel*, and from which name nickel has been derived. Except in meteoric irons, nickel does not occur native, but is a constituent of many minerals. It occurs as *niccolite*, $NiAs$; *gersdorffite*, $NiSAs$; *ullmannite*, $Ni_2S_2(AsSb)_2$; *annabergite*, $Ni_3(AsO_4)_2 \cdot 8H_2O$; and *garnierite*, $2(NiMg)_5Si_4O_{13} \cdot 3H_2O$.

134. Preparation.—The sulphide ores containing nickel are first roasted to remove the excess of sulphur and to oxidize

the iron, after which the ore is smelted in a blast furnace. This produces a matte containing from 35 to 40 per cent. of nickel and copper. This matte is then concentrated to a matte containing 70 to 80 per cent. of nickel and copper, either in a blast furnace or by means of a converter. The nickel is separated from the copper and the small amount of iron still remaining in the matte by fusion with sodium sulphate and coke in a magnesia-lined, open-hearth reverberatory furnace. While in a molten condition in this furnace the charge is poled frequently for a matter of 5 hours. Sodium sulphide is formed and this dissolves the copper and iron sulphides, and the nickel sulphide is tapped into molds. The nickel sulphide is roasted with sodium nitrate, the oxide obtained is washed, dried, and pressed into cubes with powdered charcoal and strongly ignited in clay crucibles on the hearth of a reverberatory furnace. A furnace in which this reduction can be carried on continuously has been devised and is replacing the reverberatory furnace. This furnace has vertical tubes of fireclay passing through it. The tubes are charged at the top with the nickel oxide and charcoal and the metal is drawn off at the bottom.

Another method, known as the *gas method*, consists of exposing the roasted matte to the action of water gas or producer gas at a temperature of about 400° C. The reduced metal is then exposed to a current of carbon monoxide and forms nickel carbonyl, $Ni(CO)_4$. This is then passed through chambers heated to 180° C., in which the nickel is deposited.

135. Properties.—Pure nickel is a pure silver-white metal having a specific gravity of 8.9. It is capable of taking a high polish and is malleable and ductile. It does not oxidize in dry or moist air at ordinary temperatures, melts at 1,450° C., and distils in the electric furnace. It is magnetic but loses its magnetism when heated.

Nickel is used for various industrial purposes. The steel and plating industries consume the most of the nickel produced. Small quantities are used in the manufacture of laboratory and cooking utensils. Alloys of nickel are used in coinage, jewelry, boiler and condenser tubes, and for scientific apparatus.

136. Nickel Alloys.—Nickel alloys with a great many metals and forms some very important and useful compounds. Among the most important are:

Aluminum nickel, which is composed of 28 to 30 per cent. of aluminum and from 40 to 72 per cent. of nickel, is used for cheap jewelry. Nickel slightly hardens and toughens aluminum.

Chrome nickel, which is used for making high-speed tool steel. It contains 73 per cent. of chromium, 23 per cent. of nickel, 2.5 per cent. of iron, 1 per cent. of carbon, and .5 per cent. of silicon.

Molybdenum nickel, which is also used to alloy with steel and usually contains 40 to 75 per cent. of molybdenum, 20 to 50 per cent. of nickel, 2 to 2.5 per cent. of iron, 1 to 1.5 per cent. of carbon, and from .25 to .5 per cent. of sulphur.

Invar, which is an alloy of iron and nickel containing 36 per cent. of nickel and 64 per cent. of iron, is used for the manufacture of measuring instruments. The valuable property of this alloy lies in the fact that it has no expansion when heated.

Nickel-iron alloys containing more than 36 per cent. of nickel are influenced by temperature, the coefficient of expansion increasing with the proportion of nickel.

Platinite, which is an iron-nickel alloy containing 42 per cent. of nickel, has the same coefficient of expansion as glass, and is used for making armored glass.

Ferro-nickel, which is an iron compound containing from 25 to 75 per cent. of nickel, is used to increase the elasticity and tenacity of steel. It is used in the manufacture of steel for armor plates, guns, etc.

Constantan, which is the trade name for an alloy used largely for the manufacture of resistance devices for electrical work. It contains 40 per cent. of nickel and 60 per cent. of copper.

German silver, which consists of 50 to 60 per cent. of copper, 20 to 30 per cent. of nickel, and from 20 to 30 per cent. of zinc, is a silvery-white compound used in the manufacture of jewelry, scientific instruments, resistance wires, etc.

Monel metal, which is an alloy of 3 parts of nickel to 1 part of copper, is obtained from the copper-nickel deposits of the

Sudbury district. It has a silver-white color and takes a high polish; it has a high melting point, great tensile strength, and resists corrosion, particularly by the strong acids.

Alloys of copper with nickel and zinc, or with nickel alone, are used in this country, Germany, Belgium, and Switzerland for the manufacture of small coins. The advantages of nickel coins are: (1) nickel being dearer than copper, the coins can be made smaller for the same value, and consequently they are more convenient to handle; (2) the alloy is hard and therefore wears well; and (3) its manufacture not only requires skilled workmen, but also powerful machines, facts that offer a certain safeguard against counterfeiting.

COMPOUNDS OF NICKEL

137. Nickelous and Nickelic Oxides.—*Nickelous oxide*, NiO , and *nickelic oxide*, Ni_2O_3 , are known. Nickelous oxide is an ash-gray powder that is obtained by strongly igniting the nitrate or carbonate of nickel. On adding potassium hydroxide to a nickel salt, an apple-green precipitate of *nickelous hydroxide*, $\text{Ni}(\text{OH})_2$, is formed. When heated this is converted into nickelous oxide.

Nickelic oxide, Ni_2O_3 , is a black powder prepared by the careful ignition at a low temperature of the nitrate or carbonate. *Nickelic hydroxide*, $\text{Ni}(\text{OH})_3$, is precipitated as a black powder when the solution of a nickel salt is treated with sodium hypochlorite. As nickelic oxide and hydroxide are the only compounds in which nickel acts as a trivalent element, the endings *ous* and *ic* are seldom used in speaking of the other compounds of nickel.

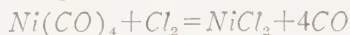
138. Nickel Chloride.—Nickel chloride, NiCl_2 , may be obtained anhydrous by the action of chlorine on nickel filings; it is volatile at a dull-red heat, and sublimes in golden-yellow scales. It may be obtained in solution by the action of boiling water on the anhydrous salt, or by the action of hydrochloric acid on either oxide or carbonate of nickel. Its solution is green, and after proper concentration deposits beautiful green crystals having the composition $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

139. Nickel Sulphate.—Nickel sulphate, $NiSO_4$, is deposited in fine emerald-green prisms, having 7 molecules of water, isomorphous with magnesium sulphate, when its solution is allowed to evaporate spontaneously below 15° C. There is another sulphate containing 6 molecules of water that is dimorphous. When deposited between 20° and 30° C. it crystallizes in octahedrons, but when its solution is made to crystallize between 60° and 70° C., monoclinic crystals are obtained isomorphous with the corresponding sulphates of zinc and cobalt. Nickel sulphate dissolves in three times its weight of water at 10° C.

140. Nickel Ammonium Sulphate.—Nickel ammonium sulphate, $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$, used in nickel-plating, is prepared by dissolving pure nickel in dilute sulphuric acid and adding ammonium sulphate to the solution. The crystalline paste formed is purified by recrystallization. It forms green, monoclinic prisms somewhat soluble in water.

141. Nickel Sulphide.—Nickel sulphide, NiS , is obtained as a black precipitate by the action of an alkaline sulphide on a salt of nickel; it is insoluble in HCl , but ammonium disulphide dissolves it to a dark-brown liquid.

142. Nickel Carbonyl.—Nickel carbonyl, $Ni(CO)_4$, is obtained when carbon monoxide is passed over metallic nickel at a temperature of about 100° C. It is a colorless liquid boiling at 43° C.; it solidifies at -25° C. and forms needle-shaped crystals. It is soluble in alcohol, benzene, and chloroform, but is insoluble in dilute acids or alkalis. Its vapor decomposes at 150° to 180° C. into nickel and carbon monoxide. Chlorine decomposes it according to the equation:



143. Nickel Carbonate.—Nickel carbonate, $NiCO_3$, is obtained as pale-green rhombohedra when a solution of nickel chloride is heated with calcium carbonate. When a solution of an alkaline carbonate is added to a solution of a nickel salt a pale-green precipitate of a basic nickel carbonate of varying composition is thrown down.

OSMIUM, IRIDIUM, AND PLATINUM

OSMIUM

Symbol Os. Atomic weight 190.9. Molecular weight 190.9. Valence II to VIII.

144. History and Occurrence.—Osmium is always present in the residue from platinum ores, in combination with iridium. In 1804 Tennant showed that the platinum residues contained the two new metals iridium and osmium, the latter so named from the Greek word meaning *a smell*, because of the peculiar odor of the peroxide. Osmium occurs in the platinum ores as an alloy of iridosmium.

145. Preparation.—Osmium is easily separated from the platinum residues by heating them in a porcelain tube through which a current of air is passed, converting the osmium into the volatile peroxide. This is then mixed with carbon monoxide and passed through a red-hot porcelain tube, when the metal is obtained in the form of a powder. By fusing the powder with tin in a graphite crucible, treating the alloy formed with hydrochloric acid, and heating the residue in a current of hydrochloric-acid gas, the crystalline variety is obtained.

146. Properties.—Osmium is a bluish-white metal, is harder than glass, and has a specific gravity of 22.48. It is almost infusible in the absence of air, but when strongly heated in the air it burns with the formation of the poisonous peroxide. Because of its high melting point, about $2,700^{\circ}\text{C.}$, osmium is used for the manufacture of incandescent electric lamps, and, alloyed with iridium, for the tips of gold pens.

147. Osmium Compounds.—Five oxides of osmium are known: the *monoxide*, OsO , a gray-black powder insoluble

in acids; the *sesquioxide*, Os_2O_3 , also black and insoluble in acids; the *trioxide*, OsO_3 ; the *dioxide*, OsO_2 , which forms a copper-colored mass which decomposes in the air; and the extremely poisonous *peroxide*, OsO_4 , which forms colorless prismatic crystals that volatilize below the boiling point of water and have an irritating vapor that affects the eyes and stains the skin black. The oxides OsO , Os_2O_3 , and OsO_2 are bases; OsO_3 forms salts with the bases, forming *osmites*, M_2OsO_4 ; and OsO_4 acts as an indifferent oxide.

Osmium dichloride, $OsCl_2$, and *osmium tetrachloride*, $OsCl_4$, are obtained as two distinct bodies when the metal is heated in chlorine; $OsCl_2$ is the less volatile, and forms green, needle-like crystals, while $OsCl_4$ is a dark-red powder.

IRIDIUM

Symbol Ir. Atomic weight 193.1. Molecular weight 193.1. Valence II, III, and IV.

148. Occurrence and Preparation.—When Tennant discovered osmium and iridium in the residues from platinum ore he found that the salts of the one metal had different colors, and to this metal he gave the name *iridium*. It is found in platinum ores alloyed with platinum and with osmium. The platinum-iridium alloy is found in the form of small cubes, whereas the osmium-iridium alloy occurs as irregular, flat grains. Iridium is prepared from the latter alloy by fusing with zinc and heating until the zinc is all driven off. The residue is then ignited with barium nitrate, the mass leached with water, and boiled with nitric acid. The iridium is then precipitated as ammonium-iridium chloride and ignited, yielding spongy iridium. This is purified by fusing with lead and treating the resulting mass with nitric acid and with aqua regia.

149. Properties.—Iridium is a white, steel-like metal with a specific gravity of 22.4. Next to osmium, it is the most difficult metal of the platinum group to fuse, and is the least volatile of this group. It melts at about $2,000^\circ \text{C.}$, is very brittle when cold, but somewhat malleable at a white heat. It

does not oxidize in the air; it is insoluble in aqua regia unless alloyed with considerable platinum. It unites with chlorine at a low red heat. Alloyed with platinum it forms a hard, elastic compound that takes a fine polish and does not tarnish.

150. Iridium Compounds.—*Iridium sesquioxide*, Ir_2O_3 , is the product of the oxidation of finely divided iridium in the air. It is a black powder insoluble in acids, begins to decompose at 800°C ., and at $1,000^\circ \text{C}$. is converted into the metal and oxygen. The *dioxide*, IrO_2 is a black powder obtained when the hydroxide is heated in a current of carbon dioxide. The *tetrachloride*, IrCl_4 , is obtained when the finely divided metal is dissolved in aqua regia. The *dichloride*, IrCl_2 , is obtained by heating a solution of the tetrachloride or by passing it over finely divided iridium heated to a red heat. The *trichloride*, IrCl_3 , is prepared by heating a double chloride with sulphuric acid.

PLATINUM

Symbol Pt. Atomic weight 195.2. Molecular weight 195.2. Valence II and IV.

151. History and Occurrence.—Platinum has been known for many centuries, but was first thoroughly investigated during the 18th century. It was first described by Watson, in 1750, and more exactly by Scheffer, in 1752, who described it as white gold. It derives its name from the Spanish *platina*, meaning little silver. It is found in nature in the metallic state in flattened grains in river sands. It is never pure, being always accompanied by the metals of this group, together with some iron, copper, and gold. The principal source of supply is the Ural Mountains of Russia, though it is also found in Brazil, Peru, Borneo, Australia, and California.

152. Preparation.—Platinum is usually prepared by wet methods. The ore is treated with aqua regia until all the platinum is dissolved and is then filtered. The filtrate is treated with lime water until only slightly acid, thus removing the iron, copper, iridium, rhodium, and part of the palladium.

The filtrate is evaporated to dryness, ignited, and then washed with dilute hydrochloric acid. The platinum thus obtained is fused with lead, and digested with nitric acid, removing any lead, copper, and other impurities. The residue is dissolved in aqua regia and the platinum precipitated with ammonium chloride. As the precipitate contains some rhodium, it is fused with potassium bisulphate, leached with water to dissolve the rhodium sulphate formed, the precipitated platinum heated to redness, and then fused into a compact form before the oxyhydrogen blowpipe.

Lately Deville and Debray devised a method that has almost completely superseded the foregoing. In this method the crude platinum is melted with lead and lead sulphide. The alloy of lead and platinum is then melted in a furnace consisting of hollowed out blocks of lime, Fig. 1, in a current of air by means of the oxyhydrogen flame, and is then cast into ingots.

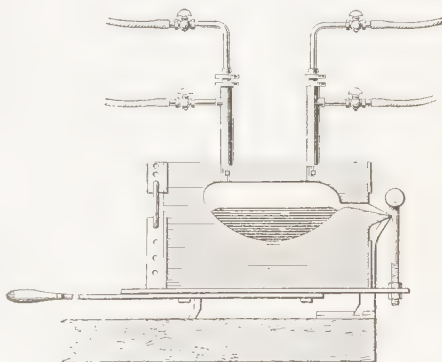


FIG. 1

153. Properties.

Pure platinum is a tin-white metal, softer than silver, but is hardened by the presence of other metals, especially iridium. It has a specific gravity of 21.48, melts at $1,775^{\circ}$ C., and can be welded at a white heat. Owing to its low coefficient of expansion, which is very nearly the same as that of glass, it can be sealed into glass without cracking the latter by unequal contraction on cooling. It is not affected by the air, is insoluble in all single acids, but alloys readily with phosphorus, silver, lead, tin, bismuth, arsenic, antimony, etc. It absorbs hydrogen at a red heat and also causes many bodies to combine with oxygen.

Its resistance to the action of acids and to high temperatures renders platinum very valuable in chemical processes. It is indispensable to the analytical chemist. It can be easily rolled

into thin foil and drawn into fine wires, it having been drawn into a wire $\frac{1}{30000}$ inch in diameter.

154. Platinum, as has already been stated, possesses the power of inducing chemical combination between oxygen and other gases to a remarkable degree. The spongy as well as the compact metal possesses this property. This can be readily shown by heating a piece of platinum foil to redness in a Bunsen burner, extinguishing the gas, and rapidly turning it on again, when the cold gas will keep the foil at a red heat, in consequence of the combination with atmospheric oxygen at the surface of the platinum.

Spongy platinum, in a very active form, is obtained by gently igniting ammonium platonic chloride. This forms a porous mass of finely divided metallic platinum, which has an extremely large surface compared with its mass.

155. Platinum Black.—When platinum is precipitated in the metallic state from solutions it forms a soft, black powder known as platinum black. It is also obtained when platonic chloride is treated with formaldehyde. This substance has the power of absorbing more than 800 times its volume of oxygen. This oxygen does not combine with the platinum, but is condensed into its pores, and is available for combination with other substances. The power of promoting combination with oxygen is so great that if it is introduced into hydrogen, the oxygen will at once unite with hydrogen and form water. After being heated to redness for a number of times platinum black becomes denser and loses considerable of its activity.

COMPOUNDS OF PLATINUM

156. Oxides of Platinum.—Two oxides of platinum are known. *Platinous oxide*, PtO , prepared by the ignition of the corresponding hydroxide, $Pt(OH)_2$, is a gray or violet powder that is converted into the metal when strongly heated. When heated with a solution of formic acid, a violent evolution of carbon dioxide occurs and platinum black is formed. *Platonic oxide*, PtO_2 , is obtained in a similar manner. *Platonic hydrox-*

ide, $Pt(OH)_4$, and *platinous hydroxide*, $Pt(OH)_2$, are obtained by treating the corresponding chlorides with sodium hydroxide. The former is acid in character and forms a few salts of the formula $M_2Pt(OH)_6$; the latter is an oxidizing agent and acts as a weak base.

157. Chlorides of Platinum.—The most important and best known salt of platinum is *platinic chloride*, $PtCl_4$. This may be prepared by heating metallic platinum in chlorine to a temperature of about $1,300^\circ\text{C}$. It may also be prepared by dissolving scrap platinum in a mixture of 4 volumes of hydrochloric acid and 1 volume of nitric acid, gently evaporating the solution to a syrupy consistency, redissolving in hydrochloric acid, and again evaporating to a syrup. (U. S. P., page 543.)

The evaporation must not be carried on too rapidly or too far, because of the possibility of forming some metallic platinum. On cooling, the liquid solidifies to a red-brown mass very soluble in water and alcohol, and absorbs moisture from the air. If the solution is allowed to crystallize before all the hydrochloric acid is expelled, brown, prismatic needles of *chloroplatinic acid*, $H_2PtCl_6 \cdot 6H_2O$, are obtained. This compound forms chloroplatinates by the replacement of the hydrogen of metals. With the alkali metals it forms salts that, owing to their great differences in solubility, are very valuable to the analytical chemist.

Potassium chloroplatinate, K_2PtCl_6 , or potassium platinic chloride, is precipitated as a yellow crystalline mass when a solution of potassium chloride is added to a solution of chloroplatinic acid. It is slightly soluble in hot water, 5 parts in 100 parts of water, and is insoluble in alcohol.

Sodium chloroplatinate, Na_2PtCl_6 , is obtained in the form of red prisms or tablets and differs from the potassium salt in being readily soluble in water and alcohol.

Ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is obtained as a lemon-yellow crystalline mass when chloroplatinic acid is added to an ammonium salt. It is sparingly soluble in water and insoluble in alcohol. When heated, it decomposes without fusion, yielding spongy platinum.

Platinous chloride, $PtCl_2$, is prepared by heating chloroplatinic acid to 300° C., when chlorine is evolved. It is also prepared by heating spongy platinum in a current of dry chlorine to 250° C. It forms a dingy green powder insoluble in water or in nitric or sulphuric acid. It is soluble in hot hydrochloric acid, yielding a red solution. Heat decomposes it into chlorine and platinum. The hydrochloric-acid solution, when added to ammonium chloride, yields a double salt, *ammonium chloroplatinite*, $(NH_4)_2PtCl_4$. The *potassium salt*, K_2PtCl_4 , forms rose-colored, crystalline fibers, and forms the starting point for the formation of *chloroplatinous acid*, H_2PtCl_4 , and its salts.

158. Iodides of Platinum.—*Platinic iodide*, PtI_4 , is a dark-brown to black amorphous substance obtained when hydriodic acid acts on a soluble chloroplatinate. It is soluble in hydriodic acid, forming the soluble, unstable compound *iodoplatinic acid*, $H_2PtI_6 \cdot 9H_2O$. *Platinous iodide*, PtI_2 , is formed as a black powder when platinous chloride and potassium iodide are boiled together.

ELEMENTS OF VOLUMETRIC ANALYSIS

VOLUMETRIC DETERMINATIONS

INTRODUCTION

VARIOUS KINDS OF ANALYSES

1. Definitions of Terms.—By the term analysis is meant the separation of a chemical compound into its constituent elements. If the purpose of the analysis is that of ascertaining what *elements* a substance contains, without reference to quantity, it is known as **qualitative analysis**.

An analysis that aims to ascertain the exact *quantities* of the different constituents of a substance is known as **quantitative analysis**. Obviously, the qualitative analysis must precede the quantitative one, for one must know what elements a substance contains before their amounts can be determined.

The methods employed in quantitative analysis vary greatly, and are based on a variety of principles. Depending on the principle employed, the subject may be divided into *gravimetric analysis*, *volumetric analysis*, and *special methods*.

2. Gravimetric Analysis.—In gravimetric analysis the elements are determined by separating them and then weighing them. The elements may be precipitated, separately, and weighed; or they may be precipitated in the form of compounds of known composition that are capable of being

accurately weighed. If the composition is not known, there are means for calculating the quantity of the desired element contained in the compound.

3. Volumetric Analysis.—Volumetric analysis is that branch of quantitative analysis in which the quantities of substances present in solutions are estimated by means of standard solutions, the strengths of which are known, in terms of the substance to be analyzed. The *volume* of the standard solution used then serves as a measure of the quantity of any particular ingredient in the substance to be analyzed.

4. Special Methods.—Under this head are grouped those methods that are based on principles differing from those already described. To this class of analysis belongs the so-called *colorimetric* methods, in which the quantity of a substance in solution is determined by comparing the color of the unknown solution with the color of a solution of known strength. Or the quantity of the substance may be determined by means of the polariscope, the extent to which the solution polarizes light indicating the percentage of the element present in the solution.

VOLUMETRIC SOLUTIONS

5. Classification.—Volumetric solutions are designated as *standard solutions*, or solutions the strengths of which are known, and *normal solutions*, which are also standard solutions, but differ in that the term *normal* signifies a definite quantity of the solid substance dissolved in a certain definite quantity of pure distilled water. Both classes of solutions are used by the analytical chemist.

6. Normal Solutions.—Normal solutions are based on equivalent weights. That is, a normal solution contains in 1,000 cubic centimeters the chemical equivalent of 1 gram* of hydrogen. Thus, in the case of a monobasic acid or a monacid base, a *normal solution* is one that contains in 1 liter a

*NOTE.—The word **gram** is spelled **gramme** in pharmaceutical literature.

weight in grams equal to the molecular weight of the compound. In the case of dibasic and tribasic acids or diacid and triacid bases, 1 liter of the solution contains a weight in grams equal to one-half and one-third, respectively, of the molecular weight of the compound.

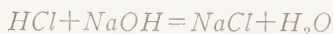
It follows that *the strength of a normal solution depends upon the valence of the active element as compared with that of hydrogen*. The valence of hydrogen being equal to 1, it is evident that if the active element is monovalent, 1 liter will contain a weight in grams equal to the molecular weight of the compound. If the active element of the compound is bivalent, a weight in grams equal to one-half the molecular weight of the compound is dissolved. If the active element is trivalent, a weight in grams equal to one-third its molecular weight is used, and so forth. In certain cases, however, the weight of the compound dissolved in making up a normal solution depends upon the reaction that takes place when the normal solution is added to the solution of the compound to be analyzed.

7. Sub-Normal Solutions.—In practical work, normal solutions are sometimes too strong to yield very accurate results. In such cases the following solutions are largely employed: Half-normal, $\frac{N}{2}$; third-normal, $\frac{N}{3}$; fifth-normal, $\frac{N}{5}$; tenth-normal, or decinormal, $\frac{N}{10}$; and for very accurate work, one-hundredth-normal, $\frac{N}{100}$. These solutions may be made up by taking one-half, one-third, etc., as the case may be, of the weight of material necessary to make a normal solution, dissolving it in water and adding water sufficient to make one liter.

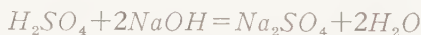
8. Preparation of Normal Solutions.—It is of vital importance that a volumetric solution is thoroughly mixed before it is used. If a solution is diluted with water, the original solution and the water tend to form separate layers, and one part of the solution will be much stronger than

another. A perfectly uniform solution is required, and this can be obtained only by very thorough agitation. The solutions must be kept in tightly stoppered bottles, for, if left exposed to the air, some solutions will absorb moisture and become weaker, but most of them lose water by evaporation, thus becoming stronger. When thus preserved, some standard solutions will keep their strength almost indefinitely, but others always decompose slowly; hence, after a solution has stood for any considerable time, its strength should always be ascertained anew before it is used. The solutions should be kept in a cool, dark place, for heat and light—especially direct sunlight—promote decomposition.

9. Advantages of Using Normal Solutions.—In general, the volumetric methods of analysis are shorter and simpler than those employed in gravimetric analysis, and in most cases the results obtained are just as accurate. One of the great advantages of this system of making solutions is the fact that all solutions thus made up have the same strength. Ten cubic centimeters of any normal acid solution will exactly neutralize 10 cubic centimeters of any normal alkali solution. Take, for example, hydrochloric-acid and sodium-hydroxide solutions. The reaction is



One molecule of one compound just neutralizes 1 molecule of the other, and as each solution contains a weight in grams equal to the molecular weight of the compound, it is evident that equal volumes of the two solutions will exactly neutralize each other. In the case of sulphuric acid and sodium hydroxide the reaction is



One molecule of the sulphuric acid unites with 2 molecules of sodium hydroxide, but as only half the molecular weight of the sulphuric acid is contained in a liter of the solution, equal volumes of these solutions just neutralize each other.

The application of the molecular weight of a compound in determining the strength of a normal solution will be made clear, further on, by a number of examples.

10. Titration.—The term *titer* refers to the *strength* of a normal solution used in volumetric analysis. Thus, when a solution is diluted it is said that its titer is decreased. **Titration** is the process by which the quantity of a constituent present in a compound in solution may be ascertained by measuring the quantity of a normal solution required to transform the constituent into another form. The stage at which the change takes place is usually indicated by a change of color, the formation of a precipitate, or by a change from an acid or alkaline to a neutral condition.

The following illustration may make the meaning of the term more clear. A sample of water contains a small quantity of sulphuric acid and it is desired to estimate the quantity of acid present in 1 gallon of the water. A definite quantity of the water is taken, placed in a beaker or flask, and a normal alkali solution is run slowly into the beaker, the contents of which are stirred continually until complete neutralization is obtained. The fact that the stage of neutralization is reached indicates that the process of titration is finished.

MEASURING VESSELS AND WEIGHING BOTTLES

11. As in volumetric analysis all determinations depend on the quantity of solutions of known strength used, it is of the utmost importance that accurately graduated measuring vessels are used in making up, and measuring out, definite quantities of these solutions. The most important of these vessels are graduated mixing cylinders, pipettes, flasks, and burettes.

12. Graduated Mixing Cylinders.—Graduated mixing cylinders are very largely used in making up standard solutions. For this purpose, a stoppered cylinder, graduated to 1 liter, as shown in Fig. 1, is generally employed, but the ordinary wide-mouth lipped cylinder is sometimes used. The form shown in Fig. 1 has an advantage in that, after the solution in the cylinder has been diluted to the required extent, the stopper may be inserted and the solution shaken, thus securing a thorough mixing.

13. Pipettes.—The pipette is generally used to transfer definite quantities of a solution from one vessel to another. The form shown in Fig. 2 is best adapted to this purpose and

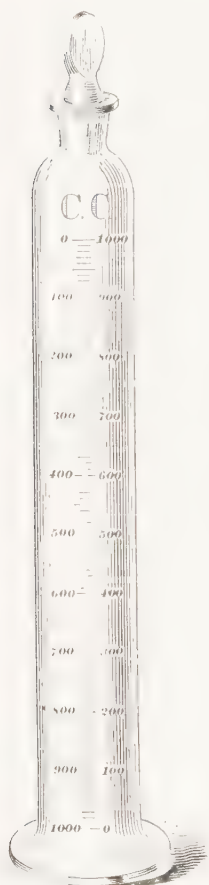


FIG. 1

is the one most largely used. In using the pipette the lower end is placed in the solution, and the air is sucked out of the pipette by applying the lips to the upper end, thus causing the solution to rise and fill it. When the solution has reached a point

somewhat above the mark, the fore-finger, which should be slightly moist, is quickly placed over the top of the pipette, thus keeping the air out and, consequently, keeping the solution in. As a rule, the solution will still stand a little above the mark on the stem; the pipette should, therefore, be revolved under the finger, thus allowing a little air to get in, until the column of liquid falls so that its surface level exactly coincides with the mark on the stem. Then, while pressing the finger firmly on the top of the burette, remove the latter to the vessel into which it is to be emptied, and lift the finger. Hold the pipette in a vertical position until the solution has run out and it has thoroughly drained; then touch the tip to the moist side of the vessel, into which the solution was emptied, to remove the last drop, which al-



FIG. 2

ways adheres to the tip of the pipette. In order to obtain uniform results when working with a pipette, the same method of using it must always be employed; and as the method just described gives consistent results, it is recommended. Beginners invariably find it difficult to handle the pipette quickly and accurately, and should prac-

tice filling it with water and emptying it until this becomes easy, before using it in handling solutions. Such practice may prevent painful injuries, caused by drawing acid or alkali solutions into the mouth.

14. In order that there may be uniformity in the results where accurate measurements are required, it is necessary to decide as to what constitutes the surface level of the liquid column in the pipette. In its narrow tube the column does not show a level upper surface but, as a result of surface tension, one of a crescent-like shape, known as a *meniscus*.

With most liquids, except mercury, the center of the meniscus is its lowest point. In judging the height of the column two readings are possible: To the top of the meniscus or to its bottom. Either one may be chosen, so long as the readings always are taken from the same point. In general, it is easier to read from the lower part of the meniscus, except in case of opaque liquids, when the top is used.

15. A pipette is very often used in cases where a sample of a substance is dissolved and separate parts of the solution are taken for different determinations. Thus, 5 grams of a substance may be dissolved in a 250-cubic-centimeter flask, and several portions of 50 cubic centimeters each may be withdrawn for the different determinations with a 50-cubic-centimeter pipette. As each of these portions contains one-fifth of the solution, each portion contains 1 gram of the substance.

Pipettes are made in various sizes. Those holding 2, 10, 15, and 100 cubic centimeters are probably the most largely used.

16. Flasks.—In making up standard solutions, the exact measurements required cannot be made in a cylinder, for a slight addition of liquid will not raise the surface of the solution sufficiently to permit of fine adjustments, hence some other



FIG. 3

measuring vessel must be employed. Undoubtedly the most convenient vessel for this purpose is an accurately graduated flask, similar to the one shown in Fig. 3. These flasks should be as narrow in the neck as is compatible with convenience in use, for the smaller the neck of the flask, the more accurately the amount of solution present may be determined; but the neck should not be so narrow as to cause inconvenience in introducing or withdrawing substances.



FIG. 4

Measuring flasks should be made of well-annealed glass, and should be rather thin, but of uniform thickness throughout, so that the danger of breaking by changes of temperature will be reduced to a minimum. They should be supplied with ground glass stoppers, and the graduation marks should fall below the middle of the neck, so that the contents of the flask can be mixed by shaking. Graduated flasks are also largely used in dissolving substances and making up the solution to a certain volume before removing parts of it with a pipette for different determinations. In making up standard solutions, a flask having a capacity of 1 liter is most largely used. Other sizes used are those having capacities of 200, 250, 300, and 500 cubic centimeters.

17. Burettes.—The instrument from which the standard solution is measured into the solution to be analyzed is known as a *burette*. This instrument has been made in a variety of forms, but only the type that is in common use will be described. The burette, Fig. 4, is fitted with a ground glass stop-cock, has a capacity of 50 cubic centimeters, or mils, and its scale is graduated into tenths of a cubic centimeter, beginning with zero at the top and ending with 50 cubic centimeters at the bottom. By starting with the burette filled to the zero mark, the reading after releasing a portion of the solution indicates the quantity of solution used in the operation. If the liquid does not stand at the zero mark at the beginning of the operation, the *first reading* of the burette subtracted from the *second reading* gives the quantity of solution used.

18. Before using the burette, Fig. 4, the stop-cock should be coated with a thin film of grease. Several kinds of greases and compositions are used in different laboratories, but ordinary vaseline, frequently renewed, will prevent sticking of the stop-cock.

The burette may be used for all kinds of solutions, and the stop-cock may be so adjusted as to deliver the solution at any desired rate. However, owing to the action of alkalies upon glass, this form of burette, when used for strong alkalies, should be immediately emptied and washed after use, or the solution will not only be partially decomposed, but will attack the stop-cock, causing it to stick, and, in a short time, to leak. Of course, such a solution should not be allowed to stand in any burette for a longer period than is necessary, since in addition to decomposing, it slowly dissolves the glass from the inside of the tube, thus rendering the graduation inaccurate.



FIG. 5

The burette may be supported by any burette stand, or clamp, that will hold it in a vertical position. The second reading should not be taken as soon as the titration is completed, but a few seconds should be allowed for the drops of liquid adhering to the sides of the burette to run down and unite with the solution. In all readings, the burette should be in a vertical position, and the eye must be on a level with the top of the liquid. The part of the burette containing liquid should not be touched with the hand unless this is necessary, as the warmth thus imparted to the liquid may be sufficient to cause perceptible expansion.

19. Weighing Bottle.—In Fig. 5 is shown a *weighing bottle* of the form generally used when weighing solids or liquids that absorb or lose water, when exposed to the air. The bottle is also used for substances that may be easily contaminated by the impure air of laboratories. This bottle is made of thin glass and is fitted with a ground glass stopper, which effectually excludes all air during the weighing operation.

SUBDIVISIONS OF VOLUMETRIC ANALYSIS

20. Classification.—The operations in volumetric analysis are usually grouped under three heads according to the object of the analysis and the character of the reactions employed. The three principal groups are as follows: (1) *Saturation*, or *acidimetry and alkalimetry*. (2) *Oxidation and reduction*. (3) *Precipitation*.

ACIDIMETRY AND ALKALIMETRY

INDICATORS

21. Purpose of Indicators.—When an acid and an alkaline solution are mixed, there is nothing in the appearance of the mixture to indicate when the *end point*, or the point of neutrality, is reached; hence the necessity of employing a substance, known as an **indicator**, that will serve to indicate when this stage is reached.

Some organic compounds, which will be described in *Organic Chemistry*, possess the property of exhibiting one color in an alkaline solution and another in an acid solution, and this property is made use of in working with acids and alkalies. Among the most common of these indicators are *litmus*, *phenolphthalein*, and *methyl-orange*, of which the latter two are now universally used, litmus being rarely used for quantitative work.

When titrating solutions of alkalies or acids, a few drops of the indicator in solution is mixed with the solution to be titrated after which the standard solution is run into it from the burette.

22. Phenolphthalein.—Phenolphthalein solutions of suitable strength may be made by dissolving 1 gram of the powder in 500 cubic centimeters of 50 per cent. alcohol. This is one of the most delicate of the indicators, and gives a very sharp reaction in all solutions to which it is applicable. In neutral

or acid solutions, this indicator is colorless, but the faintest excess of caustic alkali immediately imparts to it a bright red color. It is not applicable to solutions containing carbonates, free ammonia, or ammonium compounds, for in the presence of ammonia or carbon dioxide, the change of color does not indicate the exact point at which the reaction of the solution changes. It is one of the best, if not the best, of the indicators for solutions of the hydroxides of the fixed alkalies, and for all acids, both inorganic and organic, except carbonic acid. The fact that it can be used in alcoholic solutions, or in mixtures of alcohol and ether, renders it useful in determining organic acids which are insoluble in water. It may also be used in estimating the acids combined with many of the alkaloids.

23. Methyl-Orange.—A solution of methyl-orange, of convenient strength for use, is made by dissolving 1 gram of the powder in 1 liter of pure distilled water. It is cherry-red in an acid solution, and yellow in a solution having an alkaline reaction. This reagent cannot be used in estimating the organic acids, as the stage at which the end point is reached is not accurately indicated. This indicator, however, is not affected by ammonia or carbon dioxide, hence it is especially useful in standardizing acids by means of sodium carbonate, and as an indicator in the presence of ammonia or its salts. The change of color is not so marked as in the case of phenolphthalein, but it is very distinct if carefully handled. Too large a quantity of the indicator should not be used. Two or three drops of the solution described are sufficient for 100 cubic centimeters of solution. Nearly all of the organic indicators give a sharper reaction in cold than in hot solutions; hence, so far as possible, the solutions to be titrated should be cool, unless directions to the contrary are given. It will be noticed that either one or the other of these indicators can be used with all solutions likely to be met with in acidimetry and alkalimetry.

PREPARATION OF SOLUTIONS

24. Choice of Standard Solution.—In order to determine the acidity and alkalinity of any solution, accurate standard solutions of potassium hydroxide or sodium hydroxide and of an acid, preferably sulphuric acid, must be available. There are several methods of making up these solutions and different materials have been used as *starting points* for fundamental standard solutions, but it is recommended that oxalic acid or the sodium and potassium salts of oxalic acid be employed by those lacking experience in this class of work, since these substances are readily obtainable in the pure state and may be accurately weighed.

It is generally possible to titrate all acid and alkali solutions with only one standard solution of each kind; but it frequently happens that acid and alkali solutions are used for other processes in which some particular solution is required; hence, it is well to make up several of the solutions most frequently used. It is absolutely necessary, at all events, to have at least one acid and one alkali solution that are strictly accurate, to serve as starting points in making up all others. These standard solutions should be kept in bottles having ground glass stoppers, and a small quantity of vaseline should be rubbed on the stopper to prevent sticking. Because of the ease with which an accurate solution of oxalic acid may be prepared, this is one of the best solutions to prepare and use as a starting point for other solutions. The preparation of this solution and its application in preparing various kinds of normal solutions will now be shown by a number of examples.

25. Normal, or $\frac{N}{1}$, Oxalic-Acid Solution.—The formula for crystallized oxalic acid is $H_2C_2O_4 \cdot 2H_2O$, which shows that it is dibasic, or contains two replaceable hydrogen atoms. Therefore, by previous definition, a normal solution of this acid may be made up by dissolving a weight in grams equal to one-half the molecular weight of the acid in distilled water and then diluting the solution at the standard temperature, 20° C., to 1,000 cubic centimeters.

The molecular weight* of oxalic acid is 126.06 and in order to make up the solution, a weight equal to $126.06 \div 2 = 63.03$ grams of the crystallized acid is very carefully weighed and then dissolved and diluted as above. When the acid crystals have been weighed out and dissolved (most conveniently in a beaker), the contents of the beaker should be transferred to the mixing cylinder, the beaker rinsed out with distilled water and the rinsings also transferred to the cylinder, and sufficient water added to bring the volume up to 1,000 cubic centimeters at a temperature of 20° C. The stopper is then placed in the cylinder and the solution well mixed by inverting the cylinder several times. The solution may then be transferred to a bottle

kept well corked and labeled as $\frac{N}{1}$ *Oxalic-Acid Solution*. One cubic centimeter of this solution contains a quantity equal to $63.03 \div 1,000 = .06303$ gram of oxalic acid.

Great care must be taken in making up this solution since it is to serve as a starting point for other normal solutions and if it is made up carelessly, results obtained by the use of other normal solutions made up from it will be inaccurate.

26. Normal, or $\frac{N}{1}$, Potassium-Hydroxide Solution.

The compound potassium hydroxide, *KOH*, contains the active monovalent element potassium. Therefore, its normal solution is made by dissolving a number of grams of the compound equal to its molecular weight and diluting to 1,000 cubic centimeters at the standard temperature.

The molecular weight of potassium hydroxide being 56.11, it would apparently be a simple matter to weigh out exactly this quantity in grams and dilute to 1,000 cubic centimeters, to obtain a normal solution. But, as potassium hydroxide is deliquescent, that is, it absorbs water from the atmosphere, it is impossible to weigh out a definite quantity with any degree of accuracy, since during the process of weighing the compound would constantly increase in weight, due to the con-

*Exact molecular weights may be obtained by means of Table I. Very close approximations of the exact weights are used in this Section and may be considered sufficiently accurate for all practical purposes.

TABLE I
INTERNATIONAL ATOMIC WEIGHTS, 1920

Name	Symbol	Atomic Weight	Name	Symbol	Atomic Weight
Aluminum.....	<i>Al</i>	27.1	Molybdenum.....	<i>Mo</i>	96.0
Antimony (Stibium).....	<i>Sb</i>	120.2	Neodymium.....	<i>Nd</i>	144.3
Argon.....	<i>A</i>	39.9	Neon.....	<i>Ne</i>	20.2
Arsenic.....	<i>As</i>	74.96	Nickel.....	<i>Ni</i>	58.68
Barium.....	<i>Ba</i>	137.37	Niton (radium emanation).....	<i>Nt</i>	222.4
Bismuth.....	<i>Bi</i>	208.0	Nitrogen.....	<i>N</i>	14.008
Boron.....	<i>B</i>	10.9	Osmium.....	<i>Os</i>	190.9
Bromine.....	<i>Br</i>	79.92	Oxygen.....	<i>O</i>	16.00
Cadmium.....	<i>Cd</i>	112.40	Palladium.....	<i>Pd</i>	106.7
Cæsium.....	<i>Cs</i>	132.81	Phosphorus.....	<i>P</i>	31.04
Calcium.....	<i>Ca</i>	40.07	Platinum.....	<i>Pt</i>	195.2
Carbon.....	<i>C</i>	12.005	Potassium (Kalium).....	<i>K</i>	39.10
Cerium.....	<i>Ce</i>	140.25	Praseodymium.....	<i>Pr</i>	140.9
Chlorine.....	<i>Cl</i>	35.46	Radium.....	<i>Ra</i>	226.0
Chromium.....	<i>Cr</i>	52.0	Rhenium.....	<i>Rh</i>	102.9
Cobalt.....	<i>Co</i>	58.97	Rubidium.....	<i>Rb</i>	85.45
Columbium.....	<i>Cb</i>	93.1	Ruthenium.....	<i>Ru</i>	101.7
Copper (Cuprum).....	<i>Cu</i>	63.57	Samarium.....	<i>Sa</i>	150.4
Dysprosium.....	<i>Dy</i>	162.5	Scandium.....	<i>Sc</i>	44.1
Erbium.....	<i>Er</i>	167.7	Selenium.....	<i>Se</i>	79.2
Europium.....	<i>Eu</i>	152.0	Silicon.....	<i>Si</i>	28.3
Fluorine.....	<i>F</i>	19.0	Silver (Argentum).....	<i>Ag</i>	107.88
Gadolinium.....	<i>Gd</i>	157.3	Sodium (Natrium).....	<i>Na</i>	23.00
Gallium.....	<i>Ga</i>	70.1	Strontium.....	<i>Sr</i>	87.63
Germanium.....	<i>Ge</i>	72.5	Sulphur.....	<i>S</i>	32.06
Glucium (Beryllium).....	<i>Gl</i>	9.1	Tantalum.....	<i>Ta</i>	181.5
Gold (Aurum).....	<i>Au</i>	197.2	Tellurium.....	<i>Te</i>	127.5
Helium.....	<i>He</i>	4.00	Terbium.....	<i>Tb</i>	159.2
Holmium.....	<i>Ho</i>	163.5	Thallium.....	<i>Tl</i>	204.0
Hydrogen.....	<i>H</i>	1.003	Thorium.....	<i>Th</i>	232.15
Indium.....	<i>In</i>	114.8	Thulium.....	<i>Tm</i>	168.5
Iodine.....	<i>I</i>	126.92	Tin (Stannum).....	<i>Sn</i>	118.7
Iridium.....	<i>Ir</i>	193.1	Titanium.....	<i>Ti</i>	48.1
Iron (Ferrum).....	<i>Fe</i>	55.84	Tungsten.....	<i>W</i>	184.0
Krypton.....	<i>Kr</i>	82.92	Uranium.....	<i>U</i>	238.2
Lanthanum.....	<i>La</i>	139.0	Vanadium.....	<i>V</i>	51.0
Lead (Plumbum).....	<i>Pb</i>	207.20	Xenon.....	<i>Xe</i>	130.2
Lithium.....	<i>Li</i>	6.94	Ytterbium (Neoytterbium).....	<i>Yb</i>	173.5
Lutecium.....	<i>Lu</i>	175.0	Yttrium.....	<i>Yt</i>	89.33
Magnesium.....	<i>Mg</i>	24.32	Zinc.....	<i>Zn</i>	65.37
Manganese.....	<i>Mn</i>	54.93	Zirconium.....	<i>Zr</i>	90.6
Mercury (Hydrargyrum).....	<i>Hg</i>	200.6			

tinuous absorption of water. In order, then, to make up an *accurate* normal solution of potassium hydroxide, it is necessary that first an *approximately* normal solution be prepared and that the latter be compared with and titrated against a normal acid solution.

27. An *accurate* normal solution of potassium hydroxide is prepared in the following manner: Weigh out approximately 60 grams of potassium hydroxide instead of the 56.11 grams required, dissolve the salt and then dilute to 1,000 cubic centimeters at 20° C. Mix the solution thoroughly and then transfer 50 cubic centimeters to a burette, leaving 950 cubic centimeters in the mixing cylinder. Now, from the burette, run a quantity of exactly 10 cubic centimeters of the *KOH* solution into a beaker, and add a few drops of phenolphthalein solution, which will cause the contents of the beaker to assume a bright red color. From another burette containing the normal oxalic-acid solution, allow about 10 cubic centimeters to run into the beaker; stir the contents with a glass rod. Then allow the oxalic-acid solution to run from the burette into the beaker drop by drop, stirring constantly until the red color of the solution in the beaker turns to a pale pink, and until a point is reached when one more drop of the acid solution will entirely disperse the pink color. When this occurs the end point is said to have been reached, and the titration is completed.

Let it be assumed that 10 cubic centimeters of the *KOH* solution requires 12 cubic centimeters of the normal oxalic-acid solution for complete neutralization. This proves that the *KOH* solution is too strong and that it must be diluted to such an extent as to require 12 cubic centimeters of this solution to neutralize 12 cubic centimeters of the oxalic-acid solution. There being 950 centimeters of the *KOH* solution on hand, it is required to know the quantity of water that must be added to it so as to make its strength equal to that of the normal oxalic-acid solution. Letting x represent the total amount of the diluted *KOH* solution, its value may be found by means of the following proportion:

Ten cubic centimeters potassium-hydroxide solution is to the 12 cubic centimeters oxalic-acid solution as the remaining 950 cubic centimeters of *KOH* solution is to x . Or,

$$10 : 12 = 950 : x$$

from which

$$x = \frac{12 \times 950}{10} = 1,140 \text{ cubic centimeters}$$

It follows that it is necessary to add a quantity equal to $1,140 - 950 = 190$ cubic centimeters of water to the *KOH* solution in order that it may represent a normal solution.

28. Before proceeding any further, it is well to emphasize a certain important feature of normal solutions. It is a fundamental fact that equal quantities of all normal solutions are equivalent in their chemical actions. Thus, 10 cubic centimeters of the oxalic-acid solution are equivalent to 10 cubic centimeters of the potassium-hydroxide solution. But, and this is of importance, these solutions do not contain *the same weight in grams* of the two solutes. Thus, in the oxalic-acid solution there is $10 \times .06303 = .6303$ gram of oxalic acid; but in the potassium-hydroxide solution the amount of the solute is only $10 \times .05611 = .5611$ gram, by reason of the difference in the molecular weights.

This definite ratio between the weights of the solutes in two solutions is of vital importance in calculating the unknown amount of solute in a given solution. For instance, it was shown in Art. **27**, that 10 cubic centimeters of the unknown *KOH* solution requires 12 cubic centimeters of the given oxalic-acid solution. This proves that in the 10 cubic centimeters there must be a quantity of potassium hydroxide equal to that contained in 12 cubic centimeters of a normal solution of this compound. That is, there must be $12 \times .05611 = .67332$ gram of potassium hydroxide in the 10 cubic centimeters. This principle serves as the basis for all calculations in volumetric analysis.

29. Normal, or $\frac{N}{1}$, Sulphuric-Acid Solution.—The formula for this acid, H_2SO_4 , shows that it is dibasic; therefore, according to the definition in Art. **6**, a weight in grams

equal to one-half its molecular weight must be dissolved in water and diluted to 1,000 cubic centimeters in order to make a normal solution. But, as it is rather difficult to weigh out an exact quantity of a liquid, it is preferable to make a solution *above* normal strength and to titrate an approximately normal solution of H_2SO_4 against a normal alkali solution.

Chemically pure (C. P.) sulphuric acid, as it appears on the market, is a solution containing about 95 per cent. of the acid and has a specific gravity of 1.84. These data may in each case be obtained from the manufacturer's label.

As the molecular weight of the acid, H_2SO_4 , is 98.076, one-half of this weight in grams, or 49.38 grams, of the *pure* acid must be dissolved and diluted to 1,000 cubic centimeters. But if the acid is only 95 per cent. pure and has a specific gravity of 1.84, the following calculation must be made in order to obtain the exact amount of the 95 per cent. acid corresponding to 49.38 grams of the 100 per cent. acid:

$$49.38 : x = 95 : 100$$

or,
$$x = \frac{49.38 \times 100}{95} = 51.98 \text{ grams}$$

The value of x , or 51.98 grams, represents the quantity of the acid solution that will contain 49.38 grams of the 100 per cent. acid.

Since the specific gravity of the 95 per cent. acid is 1.84, it follows that 1 cubic centimeter weighs 1.84 grams. The corresponding volume of 51.98 grams may be found by means of the proportion

$$1 \text{ cubic centimeter} : x = 1.84 : 51.98$$

or,
$$x = \frac{51.98}{1.84} = 28.25 \text{ cubic centimeters}$$

30. As it is rather difficult to weigh out exactly this quantity of acid, the quantity of 28.25 cubic centimeters is increased to about 30 cubic centimeters of the 95 per cent. acid and this quantity is diluted to 1,000 cubic centimeters at $20^\circ C.$, so as to make a solution *above* normal strength.

NOTE.—*Always pour sulphuric acid into the water and not the water into the acid*, since in the latter case a violent reaction takes place, sometimes with explosive violence.

Having now a solution of H_2SO_4 slightly stronger than normal, the extent to which it should be diluted is determined in the same manner as in the preparation of the normal KOH solution.

Place 50 cubic centimeters of the acid solution in one burette and 50 cubic centimeters of the normal KOH solution in a second burette, then run 10 cubic centimeters of the acid solution into a beaker, add a few drops of phenolphthalein solution, and titrate with the normal KOH solution. A pale permanent pink color that cannot be dispersed upon rapidly stirring the contents of the beaker may be considered as the end point. This pink color may be more readily seen if a sheet of white paper is placed under the beaker.

The calculations to determine the extent of the dilution of the acid solution are the same as those employed in the dilution of the KOH solution.

Supposing, for instance, that 10 cubic centimeters of the H_2SO_4 solution require 10.5 cubic centimeters of the normal KOH solution and that 950 cubic centimeters of the acid solution remain in the mixing cylinder, the total amount of H_2SO_4 solution required, in order that it may become a normal solution, is found by means of the following proportion :

$$10 : 10.5 = 950 : x$$

$$\text{or, } x = \frac{10.5 \times 950}{10} = 997.5 \text{ cubic centimeters}$$

Hence, a quantity of water must be added to the 950 cubic centimeters equal to $997.5 - 950 = 47.5$ cubic centimeters at 20°C . One cubic centimeter of the $\frac{N}{1} H_2SO_4$ solution contains $\frac{49.38}{1,000} = .04938$ gram of H_2SO_4 .

31. Normal Sodium-Hydroxide Solution.—A normal solution of sodium hydroxide, $NaOH$, contains 40 grams of the salt per liter; but, as the solid rapidly attracts moisture, it cannot be weighed accurately, and consequently a solution having approximately the proper strength must be made up, and this must be standardized against the normal acid. To make this solution, weigh out 45 to 50 grams of the pure

sodium hydroxide, dissolve it in distilled water, and dilute the solution to about 1 liter. This is probably best done by placing the solid in a liter cylinder, adding about a liter of water, and agitating so that the heat generated during solution will not break the cylinder; or it may be dissolved in a beaker, and then transferred to the cylinder. When all is dissolved, standardize the solution against the sulphuric acid or the oxalic acid, using phenolphthalein as the indicator.

In this, as in every case, the solution should be allowed to cool to the proper temperature before it is standardized. As a sodium-hydroxide solution of this strength absorbs carbon dioxide quite rapidly, it should be protected from the air as much as possible while being used, and should be kept in a tightly stoppered bottle, that is nearly filled by the solution. One cubic centimeter of normal sodium hydroxide contains .04 gram of $NaOH$.

32. Normal Hydrochloric-Acid Solution.—A normal solution of hydrochloric acid contains 36.47 grams of HCl to the liter. To prepare it, make a solution rather stronger than normal and titrate this against the normal sodium-hydroxide or potassium-hydroxide solution, using phenolphthalein as the indicator.

This solution will not retain its exact strength as well as the sulphuric-acid solution, but it has the advantage that it does not form insoluble compounds with the alkaline earths, calcium, barium, and strontium, and consequently it may be used to titrate solutions containing these metals.

33. Decinormal Solutions.—Normal solutions are sometimes too strong to be used in making accurate determinations of small quantities of substances or in titrating very dilute solutions, and for these purposes solutions one-tenth as strong as the normal ones are made up. These are known as decinormal solutions, and are generally written $\frac{N}{10}$. These solutions may be made by taking one-tenth the weight of the compound used in making the normal solution and then dissolving and diluting as before, or any definite quantity of a normal

solution may be taken and diluted to ten times its volume. Decinormal solutions may be standardized against the normal solutions. Ten cubic centimeters of normal solution will, of course, require 100 cubic centimeters of decinormal solution for neutralization. This method of standardizing is not recommended, as a very slight error in measuring out the normal solution causes ten times as great an error in the decinormal one. One inexperienced in the work is therefore advised to make up a decinormal solution of oxalic acid and then standardize other decinormal solutions against this one.

USE OF NORMAL OR DECINORMAL ACID AND ALKALI SOLUTIONS

34. General Method.—On account of their convenience, these solutions are largely used in many laboratories. One of their chief advantages is that, as they are all matched, it is possible to tell the exact amount of any alkali in a solution by means of any acid solution, and vice versa, and the calculation is very simple. For instance, if it is found that 50 cubic centimeters of a sodium-hydroxide solution require 10 cubic centimeters of a normal acid solution for saturation, it is known that the first solution contains as much sodium hydroxide as would be contained in 10 cubic centimeters of a normal solution. As 1 cubic centimeter of normal solution contains .04 gram of $NaOH$, 10 cubic centimeters contains .4 gram. Therefore, the 50 cubic centimeters of sodium-hydroxide solution contain .4 gram of $NaOH$. In any case, it is only necessary to calculate the weight of a substance that would be contained in 1 cubic centimeter of a normal solution from the molecular weight of the substance, and multiply this factor by the number of cubic centimeters of normal solution required to saturate it. Only a few determinations in which these solutions are applied in practice will be described, but if the student performs these carefully he will have no trouble with other applications.

35. Determination of $\frac{N}{10}$ Hydrochloric-Acid Solution.—Measure out exactly 5 cubic centimeters of commercial

HCl acid by means of a pipette and place in a small weighed beaker, then weigh the beaker and the acid, the difference between the two weights being the weight of the acid, which is assumed to be 6 grams in the calculations that follow. Transfer the acid in the beaker to a 100-cubic-centimeter volumetric flask, rinse out the beaker and add the rinsings to the acid, then dilute to the mark, or 100 cubic centimeters. Place 50 cubic centimeters of the cooled acid solution in a burette and run 10 cubic centimeters into a small flask or beaker, add a few drops of phenolphthalein solution and titrate with a normal or a decinormal *KOH* or *NaOH* solution.

Assuming that 10 cubic centimeters of the acid solution require 40 cubic centimeters of the $\frac{N}{10}$ *NaOH* solution for neutralization, it follows that the remaining 50 cubic centimeters of the *HCl* solution require the addition of a certain amount of water to obtain the required dilution. The total amount of this solution is found by means of the following proportion:

$$10 : 40 = 50 : x$$

from which

$$x = \frac{40 \times 50}{10} = 200 \text{ cubic centimeters}$$

It follows that a quantity equal to $200 - 50 = 150$ cubic centimeters of water must be added to the 50 cubic centimeters in order that the *HCl* solution may become a $\frac{N}{10}$ *HCl* solution.

As the molecular weight of *HCl* is 36.47, 1 cubic centimeter of $\frac{N}{10}$ *HCl* must contain .003647 gram, and 200 cubic centimeters a quantity equal to $200 \times .003647 = .7294$ gram of 100 per cent. acid.

Since only 50 cubic centimeters of the original solution are used for the diluted decinormal acid solution, it follows that a quantity equal to $6 \div 2 = 3$ grams of commercial acid is contained in it. The per cent. of pure acid present in the decinormal

solution may be found by means of the following proportion:

$$.7294 : 3 = x : 100$$

$$\text{or,} \quad x = \frac{100 \times .7294}{3} = 24.31 \text{ per cent.}$$

36. Determination of $\frac{N}{10}$ Sodium-Carbonate Solution.—In this example a modified method of titration is introduced, that of *titrating back*. In some cases of titration it is found advantageous to add, for instance, a quantity of a normal acid solution in excess of that required for neutralization of the solution that is to be tested. Subsequently, this surplus acid solution is neutralized by a normal alkali solution. When this reversed titration method is employed, the chemist is said to *titrate back*. The following example will show the application of the method.

Weigh out carefully .5 gram of Na_2CO_3 , either in a small beaker or on a watch glass, then dissolve and dilute to 100 cubic centimeters. Measure, by means of a pipette, 10 cubic centimeters of this solution and place in a beaker, adding some distilled water and a few drops of phenolphthalein solution. Now run into the beaker from a burette, stirring constantly, some decinormal H_2SO_4 solution, $\frac{1}{2}$ cubic centimeter at a time, boiling after each addition until the $\frac{N}{10}$ H_2SO_4 solution is in excess of the amount required for neutralization; that is, until the pink color due to the indicator has been entirely and permanently dispersed. Record accurately the number of cubic centimeters of $\frac{N}{10}$ H_2SO_4 solution used. Now boil the solution in the beaker for at least 5 minutes, or until all CO_2 is expelled, and *titrate back* the excess of $\frac{N}{10}$ H_2SO_4 solution with decinormal KOH or NaOH solutions. An additional drop of the indicator may be required from time to time during the titration. The difference between the quantities of $\frac{N}{10}$ H_2SO_4 and the $\frac{N}{10}$ KOH solutions used gives the quantity of $\frac{N}{10}$ H_2SO_4 required to neutralize the alkali in the sample taken.

37. The 10-cubic-centimeter sample of Na_2CO_3 solution titrated contained .05 gram of Na_2CO_3 . If 12 cubic centimeters of $\frac{N}{10} H_2SO_4$ solution were used for the first titration and 3 cubic centimeters of $\frac{N}{10} KOH$ were used in titrating back, then the total quantity of $\frac{N}{10} H_2SO_4$ solution used for neutralization is $12-3=9$ cubic centimeters.

The molecular weight of Na_2CO_3 is 106.01; a normal solution, therefore, contains $\frac{106.01}{2} = 53.005$ grams per liter and a decinormal solution 5.3005 grams per liter, or $\frac{5.3005}{1,000} = .0053$ gram Na_2CO_3 per cubic centimeter.

Since equal quantities of all decinormal solutions are equivalent in their action, and since these quantities contain corresponding weight in grams of the solutes, the actual amount per 1,000 cubic centimeters depending on the molecular weight, it follows that 9 cubic centimeters of the $\frac{N}{10} H_2SO_4$ solution are equivalent to 10 cubic centimeters of the $\frac{N}{10} Na_2CO_3$ solution.

As 1 cubic centimeter of $\frac{N}{10} Na_2CO_3$ solution contains .0053 gram of Na_2CO_3 , it follows that in 9 cubic centimeters there are $9 \times .0053 = .0477$ gram. In this case 9 cubic centimeters of the H_2SO_4 solution were sufficient to neutralize 10 cubic centimeters of the Na_2CO_3 solution; hence, the latter contains the equivalent value of only 9 cubic centimeters of the $\frac{N}{10} Na_2CO_3$ solution, or .0477 gram. The corresponding quantity in the 100-cubic-centimeter solution is $10 \times .0477 = .477$ gram of Na_2CO_3 in the .5-gram sample. The per cent. purity of this sample may now be found by means of the following proportion:

$$.477 : .5 = x : 100$$

$$\text{or, } x = \frac{100 \times .477}{.5} = 95.4 \text{ per cent. of } Na_2CO_3$$

38. If methyl orange had been used as an indicator, instead of phenolphthalein, it would not have been necessary to boil the solution after each addition of $\frac{N}{10} H_2SO_4$ solution, in order to expel the CO_2 gas. It would have been sufficient to boil the solution once after the end point had apparently been reached, and then to add a few drops of $\frac{N}{10} H_2SO_4$ solution.

39. Temperature of Solutions.—When heat is generated in making up solutions for volumetric analysis as in the cases of $NaOH$, KOH , H_2SO_4 , etc., the solution must be cooled to some standard temperature and then made up to 1,000 cubic centimeters at this temperature. In all cases of titration the temperature of the solution to be titrated, containing an unknown quantity of the substance, should also be approximately that of the solution used in the standardization of the solution in the burette. In those cases where hot solutions are to be titrated, the standard solution after being cooled and diluted to 1,000 cubic centimeters has, of course, been previously standardized against a hot solution containing a known quantity of the substance.

In all titrations, it is very important that the solution in the beaker be vigorously agitated upon the addition of the standard solution, so as to insure a perfect mixture.

OXIDATION AND REDUCTION

THEORY AND APPLICATION

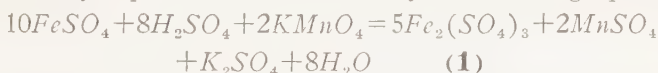
40. General Principles.—Oxidation and reduction methods of volumetric analysis may be adapted to a great many uses in analytical chemistry, the results obtained being extremely accurate if great care is exercised in the standardization of the solutions and in the subsequent manipulation.

For illustrative purposes, a few descriptive examples showing how the more common oxidizing and reducing solutions are prepared will be given. As *oxidizing agents*, potassium per-

manganate, $KMnO_4$; potassium dichromate, $K_2Cr_2O_7$; and iodine, I , are generally used, while the common *reducing agents* are ferrous sulphate, $FeSO_4$; oxalic acid, $H_2C_2O_4$; and sodium thiosulphate, $Na_2S_2O_3$.

41. The method adopted in determining the strength of an oxidizing solution may be seen from the following example, which is applied to a solution of potassium permanganate.

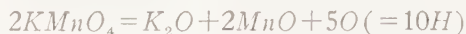
A normal solution of potassium permanganate does not contain in 1 liter a weight in grams equal to the molecular weight of the compound, but contains only one-fifth of this amount, or $\frac{158.03}{5} = 31.606$ grams. The quantity of the compound to be used in making up a normal solution depends, in this case, upon its action as an oxidizing agent, which is more easily explained and illustrated by the following equation:



It will be noted that 10 molecules of $FeSO_4$ are oxidized by 2 molecules of $KMnO_4$ or 5 molecules of $FeSO_4$ by 1 of $KMnO_4$ and upon further investigation it will be found that the valence of manganese has been reduced from 7 in $KMnO_4$ to 2 in $MnSO_4$, a difference of 5. This shows that 1 molecule of $KMnO_4$ has oxidized the equivalent of 5 H atoms. Therefore, since the strengths of normal solutions depend upon the valence of the active element as compared with the valence of hydrogen, it follows that a weight in grams equal to one-fifth of the molecular weight of $KMnO_4$ is dissolved and diluted to 1 liter.

42. Looking at the problem from the oxidation viewpoint, it will be seen from equation 1, Art. 41, that the valence of each atom of iron is increased from 2 on the left-hand side of the equation to 3 on the right-hand side. This oxidation is due to the oxygen given up by the permanganate, and in order to cause a total increase in valence of 10, five oxygen atoms are necessary. That this quantity of oxygen is given up by the $KMnO_4$ molecule may be readily seen from the follow-

ing simplified equation representing the reaction of $KMnO_4$ in a sulphuric-acid solution:



Then, since 2 molecules of $KMnO_4$ give up 5 oxygen atoms, equivalent to 10 hydrogen atoms, it follows that one $KMnO_4$ molecule gives up the equivalent of 5 hydrogen atoms. Therefore, a weight in grams equal to one-fifth of the molecular weight of $KMnO_4$ is dissolved and diluted to 1 liter in order to make up a normal solution.

43. The strength of a normal or decinormal solution of $KMnO_4$ depends upon the reaction between $KMnO_4$ and Fe , as will be seen from the following considerations: Since 1 part of the $KMnO_4$ (molecular weight 158.03) reacts with 5 parts of iron (atomic weight 55.84), a solution of $KMnO_4$ will be normal, *as far as iron is concerned*, if its strength, based upon its molecular weight, be made one-fifth; that is,



or 31.6 grams $KMnO_4$ dissolved and diluted to 1 liter gives a normal solution, and one-tenth of this weight, 3.16 grams, gives a decinormal solution.

It should be remembered by the beginner that a solution of $KMnO_4$ normal, decinormal, etc. *with respect to iron*, is not always normal or decinormal with respect to other oxidizable substances and this applies to all oxidizing and reducing agents. Therefore, in order to dispel as much as possible the confusion which may arise in the mind of the beginner when studying this subject and which can hardly be removed by an explanation, no matter how thorough, it is recommended that the equation representing the reaction between the standard solution and the solution to be titrated, always be written.

METHODS OF STANDARDIZATION

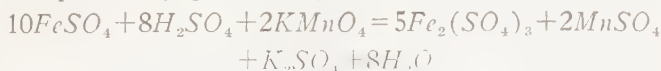
44. Standardization of Potassium Permanganate, $\frac{N}{10}$ $KMnO_4$.—Weigh out 3.5 grams of clean, dry crystals of $KMnO_4$, dissolve, and dilute to 1 liter. This solution will be slightly stronger than $\frac{N}{10}$ $KMnO_4$ and it is therefore necessary to standardize it against a reducing agent of known reducing power.

Two methods of standardizing the $KMnO_4$ will be given:

(a) With pure iron and (b) with $\frac{N}{10}$ oxalic acid.

(a) *Standardization Against Pure Iron*.—Equip four 100-cubic-centimeter flasks with rubber stoppers, and through each pass a small glass tube one-fourth of an inch in diameter or less and about 12 inches long, the upper ends of which have been previously heated and drawn out to a fine capillary opening. These tubes subsequently serve as small condensers and return condensed acid fumes to the flasks.

Weigh out very carefully four portions of iron wire of about .1 gram each, the iron content of which is known. Transfer each portion to a flask, then place each flask over a water bath and add 20 cubic centimeters of dilute H_2SO_4 made by adding one part by volume of H_2SO_4 to two parts of water. When all of the iron has dissolved, rinse the condensing tube into its flask and titrate immediately with the $KMnO_4$ solution until a faint, permanent pink color is obtained. If the results obtained by titrating the contents of the four flasks are practically the same, take the average. If not more than one shows a large variation, this one may be disregarded and the remaining three averaged. The reaction that takes place is the same as that previously given in equation 1, Art 41, that is:



The calculation to determine the strength of the $\frac{N}{10}$ $KMnO_4$ solution is performed as follows: The atomic weight of iron

being 55.84, each cubic centimeter in 1 liter must contain $55.84 \div 1,000 = .05584$ gram of Fe , if the solution is normal. If it is decinormal, as in this case, each cubic centimeter contains $.05584 \div 10 = .005584$ gram of Fe .

If the iron wire weighed out is known to contain 99 per cent. of pure Fe , the actual amount of iron present is equal to $.1 \times .99 = .099$ gram. As 1 cubic centimeter of the solution must contain .05584 gram, a quantity of .099 gram of iron will suffice for a volume of $\frac{N}{10} KMnO_4$ solution equal to $.099 \div .005584 = 17.7$ cubic centimeters. But, since the trial solution of $KMnO_4$ was made up to be slightly stronger than decinormal, it will be assumed that only 16 cubic centimeters $KMnO_4$ were required to oxidize the iron contained in the .1 gram sample, then each 16 cubic centimeters must be diluted to 17.7 cubic centimeters or the remainder of the solution in the cylinder, 950 cubic centimeters, must be diluted as shown by the following proportion:

$$16 : 17.7 = 950 : x$$

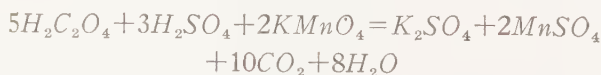
from which

$$x = \frac{17.7 \times 950}{16} = 1,050.9 \text{ cubic centimeters}$$

That is, the 950 cubic centimeters must be diluted to 1,050.9 cubic centimeters in order to make a $\frac{N}{10} KMnO_4$ solution, 1 cubic centimeter of which will oxidize .005584 gram of iron.

(b) *Standardization Against $\frac{N}{10}$ Oxalic-Acid Solution.*

Measure out 10 cubic centimeters of $\frac{N}{10} H_2C_2O_4$ solution from a burette into a beaker, add about 50 cubic centimeters of hot water ($65^\circ C.$) and a few drops of dilute H_2SO_4 and titrate with an approximately decinormal solution to a faint permanent pink color. The following reaction takes place:



Repeat the titration several times and take the average result.

Assuming that 10 cubic centimeters of the $\frac{N}{10}$ $H_2C_2O_4$ solution requires 9 cubic centimeters of $KMnO_4$ solution, and that 950 cubic centimeters of this solution remains in the cylinder, the required dilution is determined by the proportion:

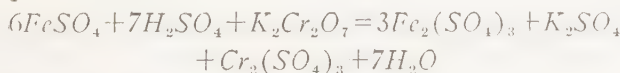
$$9 : 10 = 950 : x$$

$$x = \frac{10 \times 950}{9} = 1,055.6 \text{ cubic centimeters}$$

The 950 cubic centimeters $KMnO_4$ solution must be diluted to 1,055.6 cubic centimeters to make a $\frac{N}{10}$ $KMnO_4$ solution, and since according to Art. 43 1 liter of $\frac{N}{10}$ $KMnO_4$ contains 3.16 gram of $KMnO_4$, 1 cubic centimeter must contain .00316 gram, and 1,055.6 cubic centimeters contain $1,055.6 \times .00316 = 3.336$ grams. Since 1 cubic centimeter of $\frac{N}{10}$ $H_2C_2O_4$ contains .006303 gram of the acid, 1 cubic centimeter of $\frac{N}{10}$ $KMnO_4$ will contain a quantity of $KMnO_4$ sufficient to neutralize .006303 gram of oxalic acid; that is, .0316 gram.

NOTE.—Two different $KMnO_4$ solutions are used in the above methods for standardization.

45. Standardization of Potassium Bichromate, $\frac{N}{10}$ $K_2Cr_2O_7$.—When ferrous iron is titrated with potassium bichromate, and consequently oxidized to the ferric state, the reaction which takes place may be represented by the following equation:



From this equation it will be noted that 1 molecule of potassium bichromate oxidizes the iron contained in 6 molecules of ferrous sulphate; therefore, a weight in grams equal to one-sixth the molecular weight of potassium bichromate, 1 gram

molecule of ferrous sulphate, and this weight of potassium bichromate dissolved in water and diluted to 1,000 cubic centimeters gives a normal solution, while one-tenth of this weight is used for a decinormal solution.

The molecular weight of potassium bichromate is 294.2, then $294.2 \div 6 = 49.03$, and one-tenth of this equals 4.903.

46. To prepare the solution, weigh out accurately 4.903 grams of pure potassium bichromate, dissolve in water, and dilute to 1,000 cubic centimeters.

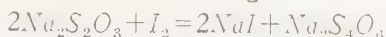
This salt has the advantage over potassium permanganate solutions in that it is permanent in solution, is readily obtained in the pure state, and may be used directly in the presence of hydrochloric acid. On the other hand, it is necessary, when titrating with this reagent, to use an *external indicator*. The indicator used is a solution of potassium ferricyanide, $K_3Fe(CN)_6$. This solution must be freshly prepared each day by dissolving a small fragment, a little larger than a pin head, in about 25 cubic centimeters of water. The solution made up in this manner should be so dilute that a drop of it when placed upon a white porcelain tile, commonly called a *spot plate*, shows only a faintly discernible yellow color.

47. The process of titration is carried on in the following manner: Prepare four samples of the iron wire and dissolve as directed for the permanganate titration; then just before each titration, dilute each sample with about five times its volume of water and titrate as rapidly as possible in order to avoid oxidation of the iron by the air.

The end point of the reaction is reached when a drop of the solution, brought in contact with a drop of the indicator on the white tile, does *not* show a blue color. In order not to run past this end point, the solution should be tested after each addition of potassium bichromate and when a point is reached where the blue color, due to the indicator, shows evidence of becoming lighter in tint, the titration must be proceeded with cautiously.

Results are calculated as for the permanganate titration.

48. Iodimetry.—The reaction on which the principles of iodimetry are based, is the following:



If sodium-thiosulphate solution is run from a burette into a solution containing an unknown quantity of iodine, to which a little starch solution has been added, the blue color due to the starch and iodine will be dispersed when all of the iodine has been reduced to hydriodic acid, HI , or its equivalent, sodium iodide, NaI , as shown by the preceding equation.

This reaction is considered one of the most sensitive in analytical chemistry and it is obvious that if a standard solution of sodium thiosulphate is available, the per cent. of iodine present in any solution may be determined. But the applicability of the method is not confined to this narrow range, since by the use of the standard solution of sodium thiosulphate all substances that set iodine free from potassium iodide may also be determined. Therefore, of iodimetric processes, it may be said, that they are not only accurate, but are also capable of wide application.

The application of the iodimetric process will be illustrated in the standardization of sodium thiosulphate.

49. Standardization of Sodium Thiosulphate.

The formula and molecular weight of sodium thiosulphate is $Na_2S_2O_3 \cdot 5H_2O = 248.2$. In practical work it is of no advantage to make up exact normal, decinormal, etc. solutions of sodium thiosulphate or iodine, since it is very difficult to keep these solutions from decomposing to a certain extent upon long standing or upon intermittent exposure to light and air. In commercial work it is sufficient to know the value of 1 cubic centimeter of the solution in terms of the substance to be titrated.

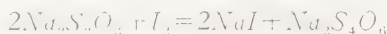
For the purpose of standardization, sodium thiosulphate is usually titrated against pure iodine, using *starch* as an indicator.

50. The *starch solution*, which is used as an indicator for all determinations involving free iodine, may be prepared as follows: Dissolve 5 grams of soluble starch in cold water, then pour this solution into 2,000 cubic centimeters of hot

water and boil for about 5 minutes. Cool and transfer the solution to a glass-stoppered bottle.

51. Before proceeding to determine the quantity of sodium thiosulphate required in a standard solution of this substance, it is convenient to introduce the terms *gram-atom* and *gram-molecule*, which mean, respectively, the atomic and the molecular weight of a substance, in grams.

From the following equation it is evident that 1 gram-molecule of sodium thiosulphate is equivalent to 1 gram-atom of iodine and this in turn is equivalent to 1 gram-atom of hydrogen.



The molecular weight of sodium thiosulphate being equal to 248.2, a decinormal solution may be made by dissolving a weight in grams equal to one-tenth of the molecular weight, or 24.82 grams, in water and diluting to 1,000 cubic centimeters. But, as this solution changes upon standing, it is advisable to weigh out a slightly larger quantity, say 25 grams, of the pure crystals and dissolve this quantity in water, diluting to 1,000 cubic centimeters and then standardizing by titrating against a known quantity of pure iodine.

52. The method of preparing the iodine solution and of employing it in titration is as follows: Into a weighing bottle, of the form shown in Fig. 5, is poured a saturated solution of potassium iodide, *KI* (2.5 grams of *KI* in 1 cubic centimeter of water). After balancing the bottle and contents on the scale pan, add about .5 gram of pure iodine. The whole is again weighed by reason of the added iodine.

The weighing bottle with its stopper is now transferred to a beaker containing a quantity of 1 per cent. *KI* solution (about 300 cubic centimeters). Removing the stopper from the bottle by means of a glass rod or other convenient device, the bottle is inverted and its contents thoroughly mixed with the *KI* solution until the iodine is dissolved. A quantity of about 2 cubic centimeters of the starch solution is now added and the solution, as prepared, may then be used for titrating against the sodium-thiosulphate solution. The end point is reached

when one additional drop of the latter solution disperses the last trace of blue color.

The amount of iodine in solution and the number of cubic centimeters of sodium thiosulphate required for titration being known, the value of 1 cubic centimeter of the sodium thiosulphate solution in terms of iodine may readily be calculated.

53. The general method of determination will now be applied to an example in which a decinormal solution of sodium thiosulphate is standardized.

The molecular weight of iodine, I_2 , is 254. Since it has been shown by the equation in Art. 51 that one atom of iodine oxidizes one molecule of sodium thiosulphate, a decinormal solution of iodine is made by dissolving 12.7 grams of iodine and diluting to 1,000 cubic centimeters; then each cubic centimeter of this solution will contain .0127 gram of iodine.

If it is now desired to make up an exact decinormal solution of sodium thiosulphate, the standard solution prepared, as above, may be titrated against iodine and correspondingly diluted so that each cubic centimeter will be equivalent to .0127 gram of iodine.

Assuming that exactly .5 gram of pure iodine were weighed out and dissolved in the KI solution referred to in Art. 52 and that 38 cubic centimeters of sodium thiosulphate solution were required for titration, it follows that each cubic centimeter of the solution is equivalent to $.5 \div 38 = .0131$ gram of iodine. As the solution should contain .0127 gram per cubic centimeter, it is seen to be slightly stronger than normal. The required volume of the $\frac{N}{10} Na_2S_2O_3$ solution is found to be equal to $.5 \div .0127 = 39.3$ cubic centimeters.

Since equal volumes of all decinormal solutions are equivalent in chemical action and as only 38 cubic centimeters of the sodium-thiosulphate solution were required, the *dilution factor* may be determined by dividing 39.3 by 38, which gives 1.034. In other words, 1 cubic centimeter of the standard sodium-thiosulphate solution, as made up, is equivalent to 1.034 cubic centimeters of decinormal solution, so if 950 cubic centimeters

of the standard sodium-thiosulphate solution remain, it must be diluted to $950 \times 1.034 = 982.3$ cubic centimeters in order to make it decinormal. Or the following proportion may be used :

$$38 : 39.3 = 950 : x$$

from which

$$x = \frac{39.3 \times 950}{38} = 982.5 \text{ cubic centimeters}$$

The slight discrepancy between the two results obtained is due to the fact that the dilution factor was carried out only to three decimal places. However, the results obtained by it are sufficiently accurate for ordinary work.

54. Standardization of $\frac{N}{10}$ Iodine Solution.—A solution is made up by dissolving about 12.8 grams of pure iodine in a saturated solution of *KI* and diluting to 1,000 cubic centimeters. This solution is then standardized against a decinormal sodium-thiosulphate solution.

PRECIPITATION

CHLORINE

55. General Principles.—A salt may be thrown out of its aqueous solution by the addition of some substance that mixes with, or is soluble in, the water and that, while without any chemical action on the dissolved salt, will reduce the solvent action of the water, as regards the salt. A precipitation may also be formed as a result of a chemical combination between the salt and the substance introduced into the solution. The determination of chlorine will illustrate the application of precipitation to chemical analysis, for which purpose a silver-nitrate solution is employed.

56. Preparation of the Silver-Nitrate Solution. Dissolve a quantity of exactly 5.846 grams of pure, dry sodium chloride in water, and dilute to 1,000 cubic centimeters in the mixing cylinder, thus obtaining an $\frac{N}{10}$ sodium-chloride solution. Then make an approximately decinormal solution of

silver nitrate by dissolving about 17.5 grams of pure silver nitrate ($AgNO_3 = 169.8$) in water and diluting to 1,000 cubic centimeters. From a burette measure a definite quantity of the decinormal sodium-chloride solution, say 10 to 15 cubic centimeters; add two or three drops of a saturated solution of pure potassium chromate in water to serve as an indicator, and dilute the solution with about 50 cubic centimeters of pure water.

From a second burette, slowly introduce the silver-nitrate solution during constant stirring. As each drop of the silver-nitrate solution falls into the sodium-chloride solution, a red spot is formed owing to the formation of a small quantity of silver chromate. Upon stirring, the silver chromate is decomposed by the sodium chloride and the red spot disappears. As the end point is approached the red color disappears more and more reluctantly, until finally the liquid assumes a permanent red color. This shows that all the chlorine has been precipitated and that a slight excess of silver has been formed, which has united with the potassium chromate to form red silver chromate.

57. The addition of silver-nitrate solution should be stopped as soon as a permanent reddish tint is produced in the solution, and the quantity of solution required to saturate the given quantity of decinormal solution should be noted. From this it is possible to calculate how much the silver-nitrate solution must be diluted, in order that 1 cubic centimeter of it will be equivalent to 1 cubic centimeter of the sodium-chloride solution. This dilution will produce a decinormal solution of silver nitrate, of which each cubic centimeter should contain .0169 gram of silver nitrate, which quantity is equivalent to 1 cubic centimeter of a decinormal sodium-chloride solution containing .00354 gram of chlorine.

58. Determination of Chlorine.—After the preparation of an accurately standardized silver-nitrate solution, it is possible to determine the quantity of chlorine present in any soluble chloride. Sodium chloride being easily obtained in a pure state is chosen as the one to use for practice.

Weigh out from .2 to .3 gram of pure, dry sodium chloride, and dissolve it in about 60 cubic centimeters of water, in a beaker. Care should be taken that this solution shall have as nearly as possible the same volume as the solution used in standardizing the silver-nitrate solution. Add 2 to 3 drops of potassium-chromate solution, and titrate with the silver nitrate in the same manner that the titration was performed in standardizing the solution, taking care to add the standard solution until the same shade of red is obtained in the solution that was produced when standardizing. The number of cubic centimeters of solution used multiplied by the decinormal factor for chlorine (.00354) gives the weight of chlorine in the sample, and from this the percentage is obtained in the usual manner.

As silver chromate is soluble in both acids and alkalies, the solution in which chlorine is determined by this method must be neutral or very nearly so. If strongly alkaline, it should be nearly neutralized with pure nitric acid before titration, and if acid, it should be neutralized with sodium carbonate. As it is better to have the solution slightly alkaline than acid, it is best to add a very slight excess of sodium carbonate when neutralizing with this reagent. Sodium salts interfere less with the reaction than ammonium or potassium compounds, hence sodium carbonate should always be used in neutralizing an acid solution for this purpose. If too much of the silver solution has been added, this may be remedied by adding 1 cubic centimeter of decinormal sodium-chloride solution, titrating again with silver nitrate, and subtracting 1 cubic centimeter from the total amount of silver-nitrate solution used.

REVIEW

ACIDIMETRY AND ALKALIMETRY

59. Purpose of Review.—When, as in the preceding pages, so many detailed explanations are intermingled with others that refer to main principles and laws, there is a possibility that some portions of the subject may be confused with other portions not directly related to one another.

It is the purpose of the succeeding condensed review to bring out the more important points and thus assist in clarifying any confused impressions.

60. Strength of Standard Solutions.—In making up a standard solution for volumetric analysis, it is evident that the number of grams of the substance to be contained in 1,000 cubic centimeters of water, that is, whether a normal, decinormal, etc. solution is required, will depend upon the purpose for which it is to be used.

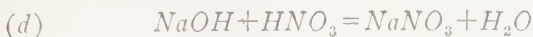
61. Examples of Normal Solutions.—The following equations refer to standard solutions of (a) hydrochloric acid, (b) sodium hydroxide, (c) sulphuric acid, (d) nitric acid, and (e) barium hydroxide.



One gram-molecule of hydrochloric acid and one of sodium hydroxide completely neutralize each other, so a weight in grams equal to the molecular weight of either substance dissolved in water and diluted to 1,000 cubic centimeters gives a normal solution.



One gram-molecule of sulphuric acid reacts with two gram-molecules of sodium hydroxide, or one-half gram-molecule of sulphuric acid completely neutralizes one gram-molecule of sodium hydroxide. Therefore, a weight in grams equal to one-half of the molecular weight of sulphuric acid is dissolved in water and diluted to 1,000 cubic centimeters.



A weight in grams equal to one gram-molecule of nitric acid dissolved in water and diluted to 1,000 cubic centimeters gives a normal solution.

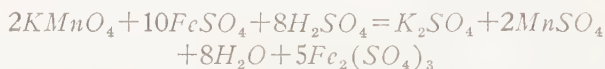


One-half gram-molecule of barium hydroxide neutralizes one gram-molecule of hydrochloric acid; therefore, a weight in grams equal to one-half the molecular weight dissolved in water and diluted to 1,000 cubic centimeters gives a normal solution.

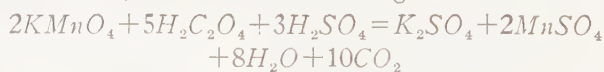
OXIDATION AND REDUCTION

62. Examples of Normal Solutions.—The following equations refer to standard solutions of (a) potassium permanganate, (b) potassium dichromate, (c) sodium thiosulphate, and (d) iodine.

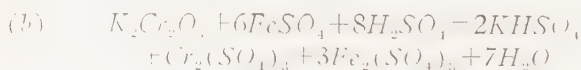
(a) Two methods are shown by means of which a standard solution of potassium permanganate may be prepared, one by means of ferrous sulphate and the other by means of oxalic acid.



One gram-molecule of potassium permanganate oxidizes five gram-molecules of $FeSO_4$; therefore, one-fifth of a gram-molecule of potassium permanganate oxidizes one gram-molecule of ferrous sulphate and a weight in grams equal to one-fifth of the molecular weight of $KMnO_4$ dissolved in water and diluted to 1,000 cubic centimeters gives a normal solution.



One gram-molecule of potassium permanganate oxidizes two and one-half gram-molecules of oxalic acid, containing five replaceable hydrogen atoms; therefore, a weight in grams equal to one-fifth of the molecular weight of $KMnO_4$ is dissolved in water and diluted to 1,000 cubic centimeters to make a normal solution.



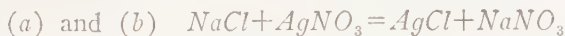
One gram-molecule of potassium dichromate oxidizes six gram-molecules of ferrous sulphate; therefore, a normal solution of $K_2Cr_2O_7$ may be made up by dissolving in water a weight in grams equal to one-sixth of its molecular weight and diluting to 1,000 cubic centimeters.



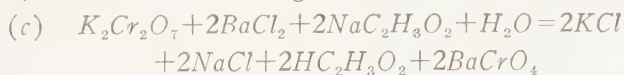
One gram-molecule of sodium thiosulphate reduces one gram-atom of iodine, which is equivalent to one gram-atom of hydrogen; therefore, in order to prepare a normal solution, dissolve in water a weight in grams equal to the molecular weight of sodium thiosulphate and dilute to 1,000 cubic centimeters. In the case of iodine, the molecular weight of which is 253.8, dissolve in water a weight in grams equal to the atomic weight (126.9) (saturated KI solution) and dilute to 1,000 cubic centimeters.

PRECIPITATION

63. Examples of Normal Solutions.—Three examples of normal solutions used in precipitation are given: (a) Sodium chloride, (b) silver nitrate, and (c) potassium dichromate.



A weight in grams equal to one gram-molecule of either sodium chloride or silver nitrate dissolved in water and diluted to 1,000 cubic centimeters gives a normal solution.



One gram-molecule of potassium dichromate precipitates two gram-molecules of barium chloride, which is equivalent to four gram-atoms of hydrogen, since barium is divalent. Therefore, in this case, a weight in grams equal to one-fourth the molecular weight of potassium dichromate dissolved in water and diluted to 1,000 cubic centimeters gives a normal solution.

PHYSIOLOGY

THE HUMAN ORGANISM

THE SKELETON

INTRODUCTION

1. Definitions.—Referring in particular to the human organism, **anatomy** may be defined as the science dealing with the structure of the human body, and **physiology**, as the science dealing with the functions of the body. **Hygiene** is the science that treats of the conditions necessary to insure the proper functioning of the human organism.

2. Cellular Structures.—The body is built up of minute structures known as *cells*. A **cell** consists mainly of a transparent, jelly-like material known as *protoplasm*. In each cell is a small centrally located body, termed a *nucleus*, which is surrounded by a number of minute granules. The latter, together with the enclosing protoplasm, is known as *cytoplasm*. A typical cell with its nucleus is shown in Fig. 1 (a).

The cells multiply by division in the manner shown in Fig. 1 (a) to (h). In view (a) is seen the centrally located nucleus and above it a small structure, known as an *attraction-sphere*, which contains two little bodies called *centrosomes*. The cell division begins with a division of the attraction-sphere into two parts, each carrying a centrosome and placing themselves at opposite sides of the nucleus, as shown in view (b). The process of division is now continued in the manner shown

in views (c) to (g), the cell contracting more in a horizontal direction, while two nuclei are being formed, until finally, as seen in view (h), it divides into two parts, each a complete cell having its own nucleus and attraction-sphere in which, eventually, twin centrosomes appear.

3. Tissues.—Combination of similar cells are known as **tissues**. As there are different kinds of cells, so there are also different kinds of tissues. Thus, muscle tissue is made of



FIG. 1

muscle cells, nerve tissue of nerve cells, kidney tissue of kidney cells, etc., each kind of tissue performing its special function.

4. Organs.—Tissues are combined to form *organs*. An **organ** is a part of the body intended to perform a definite function. For instance, the stomach is an organ for storing and digesting food; the eye, an organ for seeing; the nose, an organ for smelling and for preparing the air suitable for reception by the lungs, etc. Some organs consist of only one kind of tissue, as, for instance, the active portion of the kidney; other organs are composed of more than one kind, as the foot, which consists of bones, connecting tissue, muscle, nerves, and skin.

THE AXIAL SKELETON

5. Function of the Skeleton.—The human body is composed of a head, a trunk, and two pairs of limbs. The main portions of the body being soft and elastic, means must be provided for maintaining the parts in correct relative positions, for providing suitable support, for protecting them from external injury, and to serve as levers for moving the body and its limbs from place to place. These functions are performed by a bony structure known as the *skeleton*.

6. Principal Portions of Skeleton.—In the adult skeleton there are 206 distinct and separable bones, variously grouped. The skeleton may be divided into two main portions, the *axial* and the *appendicular*. The **axial skeleton** comprises the skull, the vertebral column, or back bone, the breast bone, the ribs, and the hyoid bone, a small bone near the base of the tongue. The **appendicular skeleton** comprises the upper and the lower limbs.

7. The Skull.—The bones of the skull, Fig. 2, may be divided into those of the brain case, eight in number, and those of the face, fourteen in number. With the exception of the lower jaw, they are all very firmly joined together, forming a strong case for the protection of the brain, ears, eyes, nose, and tongue. The bones forming the top of the brain case are thick and curved so that, in general, they are sufficiently strong to resist any blows aimed at the head and to transform them into glancing blows.

8. The Vertebral, or Spinal, Column.—The skull is supported by a column of bone called the **vertebral column**, **spinal column**, or **spine**, which extends from the head to the *haunch*, or *hip bones*. This column, which is shown in Fig. 2, and in a sectional side view in Fig. 3, consists of thirty-three bones called **vertebræ**, of which the upper twenty-four are known as *true vertebræ*, and the lower nine as the *false vertebræ*. Between each pair of true vertebræ there is a pad of *cartilage*, or *gristle*; which acts as a buffer; it also prevents

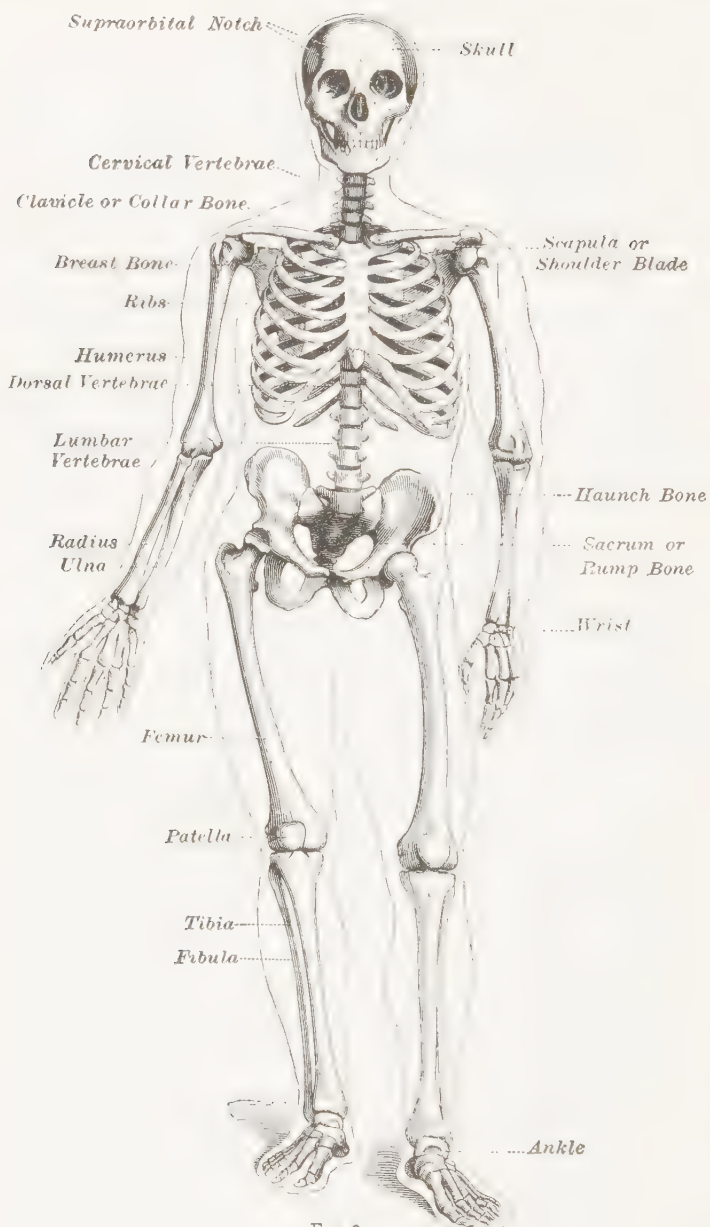


FIG. 2

the bones from jarring when they move and gives elasticity to the whole column. The spinal column contains and guards the *spinal chord*. Man and animals that have a vertebral column are known as **vertebrates**.

The vertebræ are kept in their places by bands of a tough, strong substance called *fibrous tissue*, which passes around them in all directions. Although the relative movement between any

two vertebræ is very small, the spine, as a whole, is very flexible and can be bent in every direction, the greatest amount of movement being in the neck and in the loin portions.

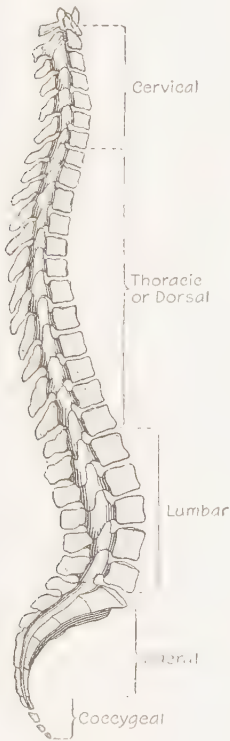


FIG. 3

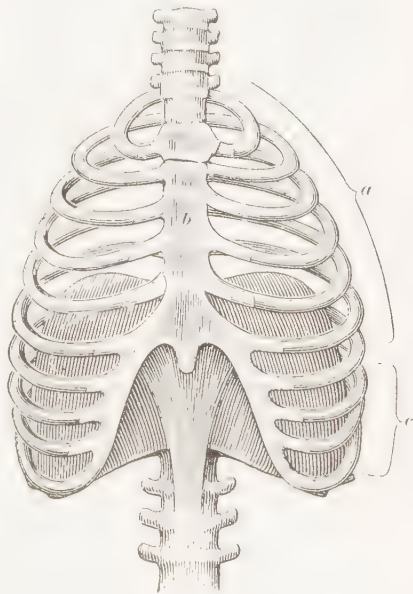


FIG. 4

9. The seven upper bones of the spinal column are called the *cervical*, or *neck*, *vertebræ*; the next twelve, the *thoracic*, *dorsal*, or *back*, *vertebræ*; and the next five, the *lumbar*, or *loin*, *vertebræ*. The succeeding five bones are known as the *sacral*, or *false*, *vertebræ*; they are to some extent fused together so as to form the *sacrum*, or *rump bone*. This is

attached to the hip bones, which connect in front and form a very strong case, called the *pelvis*; this serves to protect the bladder, intestine, etc. Finally, there are four or five bones that constitute the skeleton of a rudimentary tail and are known as the *coccygeal vertebræ*. As seen from Fig. 2, the cervical and lumbar vertebræ are entirely free, but the dorsal vertebræ are joined to the *ribs*.

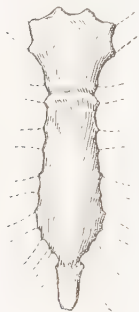


FIG. 5

10. Ribs and Sternum. — There are twelve pairs of **ribs** shaped like half loops, all being joined to the vertebral column. The seven upper pairs at *a*, Fig. 4, known as *true ribs*, are joined to the *breast bone*, or *sternum*, shown at *b*. The five lower pairs are known as *false ribs*; of these the upper three pairs, shown at *c*, are not joined to the sternum, but are attached to the seventh pair by means of a ligament. The two lower pairs of ribs are not connected with the sternum at all and are not seen in Fig. 4, but may be found in Fig. 2. These ribs are known as *floating ribs*. The sternum is shown separately in Fig. 5, the adjoining ends of the ribs being shown in dotted lines. The shaded dome-shaped muscle, seen in Fig. 4, represents the diaphragm.

The axial skeleton supports the trunk, which contains a large cavity, divided by the diaphragm into an upper and a lower cavity. The upper one is known as the *thoracic*, or *pleural*, *cavity*; also, as the *thorax*. The lower cavity is called the *abdominal*, or *peritoneal*, *cavity*.

THE APPENDICULAR SKELETON

11. Bones of Thigh and Leg.—On the outside of the hip bone, Fig. 6, there is a deep, cup-like depression that receives the rounded head of the **femur**, or **thigh bone**, the largest bone in the body. The other end of the femur rests on the *tibia*, or *shin bone*, and forms the *knee joint*, as shown in Fig. 6, the knee joint being protected by a bone called the *patella*, or *knee cap*.

The **leg**, which is also shown in Fig. 7, has two bones. The inner one, the *tibia*, is very strong and supports the entire weight transmitted by the thigh; the outer one, the *fibula*, or *brooch bone*, is a thin one which, along with the tibia, forms the ankle joint. The fibula strengthens the leg without adding much to its weight.

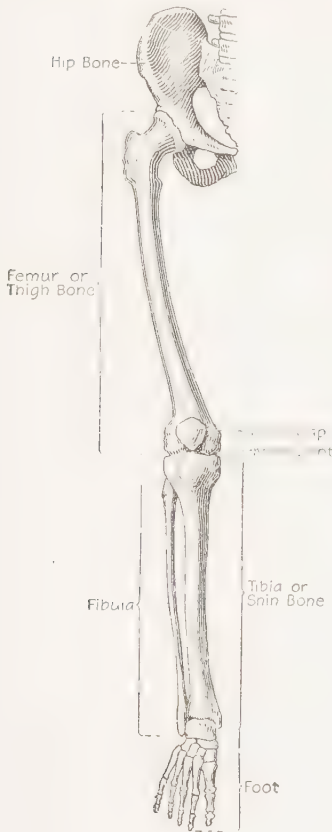


FIG. 6

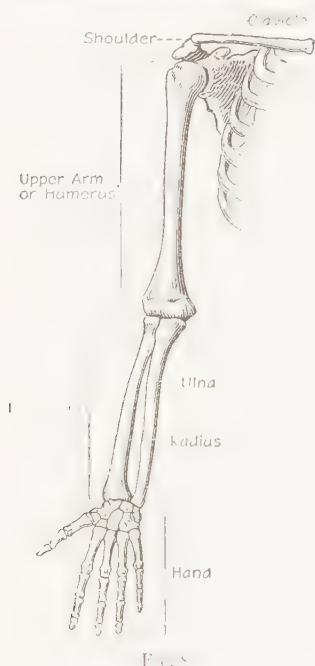
12. The Foot.—At the lower ends of the leg bones are the *ankle bones*, forming an arch, Fig. 7, that receives the upper part of one of the bones of the foot, as shown in Fig. 6. In the foot there are twenty-six thick bones, joined together very firmly and arranged



FIG. 7

in a double arch, one arch extending from the heel to the toes, the other curving transversely from side to side. This arrangement gives elasticity and strength to the foot and enables a person to move freely and easily. All the bones in the lower limbs are strong and thick, as they have to support the whole weight of the body.

13. Clavicle and Scapulæ.—Between the top of the breast bone and the shoulder, on each side, there extends, as



seen in Figs. 2 and 8, a flat, double-curved bone, called the **clavicle**, or **collar bone**, which serves to keep the shoulders apart. The **scapulæ**, or **shoulder blades**, are large, flat, irregular-shaped bones that lie on the back of the thorax, covering the seven upper ribs. The outer end of the clavicle, with a portion of the shoulder blade, forms a cavity in which the upper end of the arm bone is lodged. The shoulder blades give additional strength to the thorax and serve for the attachment of the muscles that move the upper limbs.

14. Arms and Hands.

The bones in the arms are long, thin, and light, as they have no weight to support, but are

required mainly for reaching and grasping. They correspond in number with those in the lower limbs, but are arranged somewhat differently. In the upper arm, Figs. 8 and 9, there is one bone, the *humerus*; in the forearm there are two, the *ulna* on the inside and the *radius* on the outside. These join the *wrist*, in which there are eight small bones joined firmly to each other and forming a very flexible joint.

In the hand, Fig. 8, there are nineteen bones, five being in the palm and the remaining fourteen in the fingers.



FIG. 9

15. Joints.—When two or more bones come together they form a **joint**, which may be *movable* or *immovable*. **Immovable joints** are found in the body where movements

between the bones are not necessary, such as the bones of the cranium. A **movable joint** is usually a modification of a ball-and-socket joint or of a hinge joint. The ends of the bones are enlarged to form the joint and they are coated with a layer of *cartilage*, or *gristle*, which acts as a buffer and prevents pain, when the bones move on each other. Over this cartilage there is a skin, or membrane, that gives out an oily fluid which lubricates the parts and enables them to move freely. The bones are kept in place by a number of bands of fibrous tissues, called *ligaments*, that completely surround their ends.

16. Composition of Bone.—Bones are composed of two forms of matter, animal matter and mineral matter. About two-thirds of the weight of the average bone is mineral matter and one-third animal matter. In childhood there is a smaller proportion of mineral matter in the bones, and in old age the amount of animal matter is very small. The mineral matter gives the strength to the bone and the animal matter the required flexibility. The cavities of bones are filled with *bone marrow*, and the exterior is covered with a thin membrane called the *periosteum*.

THE MUSCULAR SYSTEM

CLASSIFICATION AND COMPOSITION OF MUSCLES

17. Classification of Muscles.—The movements of the various parts and organs of the body are brought about by the muscles, which constitute the soft, fleshy part of the body and which are characterized by a special structure and by a special function of contracting in length under the influence of a proper stimulus. There are three classes of muscles: (1) the *striated*, or *striped*, and usually *voluntary muscles*, to which class the muscles attached to the skeleton belong; (2) the *unstriated*, *involuntary muscles* found in the walls of the blood vessels and hollow viscera, or internal organs; and (3) the *cardiac muscles*, which are striated, but involuntary, and of which the substance of the heart is composed.

18. Composition of Muscles.—A typical **striated muscle** consists of a fleshy mass enveloped in a membranous covering and provided at its extremities or borders with *membranes* or *tendons* by which it is attached to the bone or cartilage. Each muscle is made up of a number of fiber bundles arranged in different ways in different muscles, some of the fibers attaining a length of $1\frac{1}{2}$ inches. These bundles are connected together by a delicate tissue, which is continuous externally with the membrane covering the muscle. By means of these membranous envelopes, the bundles of muscle are brought into firm and intimate relation with the bony or other attachments of the muscle. Therefore, when the muscle contracts, it can produce a precise and definite effect on the member to be moved. The striated muscles are known as *voluntary muscles* because they are under control of the will, their action being governed by the brain.

19. The **unstriated muscles** have no tendons, but form extended membranes that surround cavities of various forms, such as the blood vessels, intestines, stomach, etc. These muscles are not controlled by the will, but by certain nerve centers, and are therefore known as *involuntary muscles*. They are composed of short, thin, pointed cells bound together by an animal cement and held in place by a network of connective tissue. These cells, which are of an average length of $\frac{1}{600}$ inch, contain a protoplasm that may contract longitudinally. They are usually arranged transversely about a cavity; hence, their contraction results in a reduction of the cavity opening.

20. The **cardiac muscles** may be considered as a combination of striated and unstriated muscles. The nucleated and branched cells are combined into a network surrounding the heart. While also these muscles show striations, they are less prominent than in the regular striated muscles and the degree of constriction is also less than that of the latter muscles.

21. Axial and Appendicular Muscles.—The striated muscles attached to the skeleton may be divided into two series: (1) *axial muscles*, and (2) *appendicular muscles*. The **axial muscles** are arranged and grouped around the axial skeleton

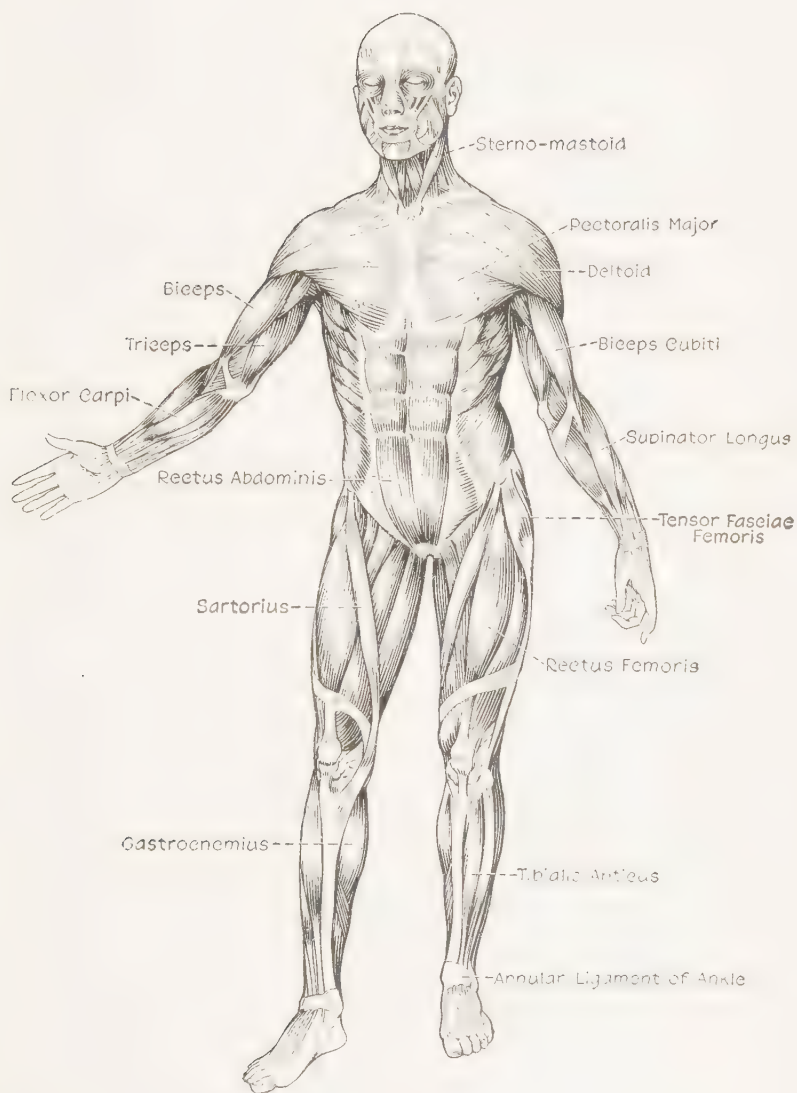


FIG. 10

and comprise the muscles of the trunk, head, and face. The **appendicular muscles**, the muscles of the limbs, are grouped around the appendicular skeleton. Fig. 10 is a front view of the human body in which the principal muscles are indicated. Some of the more prominent muscles are given their Latin names.

The principal functions of the muscles of the body are as follows: (1) To move the body organs and limbs, as in walking, turning the eyes, expanding the lungs, operating the heart, etc. (2) To assist the bones in enclosing the body cavities for the purpose of protecting the organs contained in them. (3) To assist the ligament at a joint in holding the bones in position.

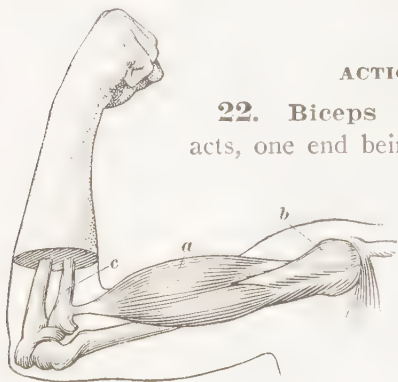


FIG. 11

ACTION OF MUSCLES

22. Biceps Muscle.—When a muscle acts, one end being fixed, the middle portion of the muscle shortens and swells and draws its free end toward the fixed one. This is clearly shown in Fig. 11, which shows the covering and some of the muscles removed from the upper arm and a portion of

the lower arm, so as to show the action of the biceps muscle *a*. The upper end of this muscle is attached at *b* to the humerus, and the lower end at *c* to the radius. The illustration shows how the contracting biceps muscle moves the lower arm and enables it to lift a load supported by the hand.

DIGESTION

PURPOSE AND CLASSIFICATION OF FOODS

23. Foods and Energy.—The latent energy of coal is transformed into heat in the firebox of a locomotive and by evaporating the water in the boiler it furnishes the necessary power for pulling the train. In the same manner the food absorbed by the human body acts as a source of power for performing work. But, there is a great difference between the two cases in that the food assimilated by the human organism not alone has to furnish power, but has to provide material for necessary repairs; has also to supply the various substances needed for growth; and, finally, has to supply the fuel for maintaining the temperature of the body at a point where the body is able to perform its functions in the most efficient manner.

There is also this difference between the two cases, that if in the case of a machine its source of power is cut off, it ceases to work, whereas the human organism, for a time, will perform its functions by consuming its own substance. But, finally, this source of energy will also be exhausted and the body will cease to live.

24. Classification of Foods.—The food that supplies the body with the necessary energy is of many varieties, but may, however, be divided into the following three great classes: (1) *Carbohydrates*; (2) *fats*; and (3) *proteids*.

The **carbohydrates** include the starches and sugars. Almost all of them come from plants and nearly every plant has its own kind of starch; for instance, corn starch, wheat starch, potato starch, arrowroot starch, and many other varieties. Sugar is an independent food derived mostly from sugar cane and sugar beets.

In the group of **fats** are included various oils. There is no difference between these fats and oils, except that at ordinary temperatures the oils are liquid. Among the fatty foods are included butter, lard, the fat of meat, cottonseed oil, olive oil,

etc. The carbohydrates and the fats are fuel foods oxidized in the cells to supply energy to the body.

Proteids are contained in most of the foods derived from animals. The proteids include lean meat, fish, eggs, milk, and cheese. The proteids provide largely the material required for building the living cell.

In addition to these foods the body must have a constant supply of oxygen from the air; also water and certain minerals, such as salt, etc.

THE DIGESTIVE PROCESS

25. Digestive Organs in General.—Before the human organism can obtain any benefits from the different foods supplied to it, these foods must be subjected to certain preparatory processes to render the foods fit for assimilation by the body. These processes are included in the common term **digestion**, and the organs that perform the various processes of digestion are known as **digestive organs**. Among these organs are also included those that constitute the upper part of the *alimentary canal*, such as the

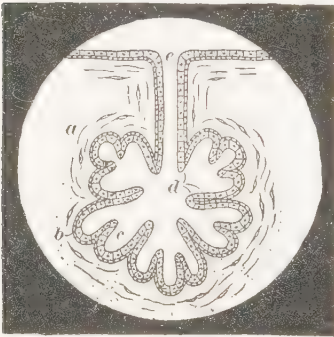


FIG. 12

mouth, with its teeth, tongue, etc. The action of the digestive organs is supplemented by the actions of such organs as the *liver*, the *pancreas*, and various *glands*.

26. Numerous organs in the body may be classified as **glands**, such as the *salivary glands*, the *liver*, the *pancreas*, etc. A typical form of gland is shown in Fig. 12. It is seen to consist of *lobes a*, which are divided into smaller portions *b*, known as *lobules*. The cavities shown at *c* are known as *alveoli*; they are covered with secreting cells *d*.

The gland absorbs water and other substances from the blood and converts them into certain fluids which it delivers

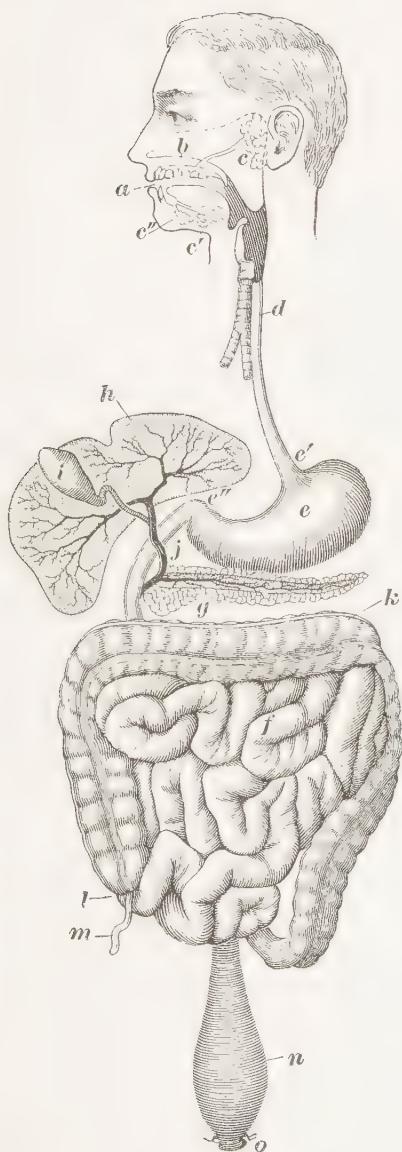


FIG. 13

through the duct *c*. When a gland is delivering the fluid produced, it is said to *secrete*, and the fluid is known as a *secretion*. Glands without outlets are known as *ductless glands*.

27. Alimentary Canal.—The alimentary canal, represented in Fig. 13, is nearly 30 feet in length. Its principal divisions are: the mouth, pharynx (throat), æsophagus, stomach, and the small and large intestines. In the walls of this canal there are unstriated muscles that periodically contract and force the food toward the exit of the intestines. The canal is lined with a thin coating known as the *mucous membrane*. The various organs along the alimentary canal may be considered as a series of chemical laboratories in which raw materials are transformed and refined by the action of suitable chemical reagents.

28. The Mouth. Crushing and grinding of the food partaken of takes place in the mouth *a*, Fig. 13, by means of

teeth *b*; simultaneously, the food is mixed with *saliva*. There are four kinds of teeth: (1) *Incisors*; *canines* or *cuspid*s; *bicuspid*s; and *molars*. The sharp **incisors** serve for biting off food and in this work they are assisted by the **cuspid**s. The **bicuspid**s and **molars** with their wide surfaces act as food crushers.

Cross-sections of an incisor and a molar are shown in Fig. 14 at (a) and (b), respectively. They show that a tooth is composed of a *crown*, a *neck*, and one or more *roots*. The latter stand in sockets in the jaw-bones and are held in place by a hard bone-like cement. The outer coat of the crown is known as the *enamel*. Under the enamel, and forming the main bulk of the tooth, is the *dentine*, a very hard substance. In a central

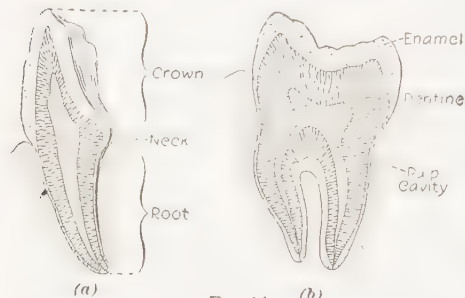


FIG. 14

chamber, known as the *pulp cavity*, is a loose tissue containing nerves and blood vessels which enter the cavity through a small opening in the tip of the root.

29. Salivary Glands.—

There are six **salivary glands** arranged symmetrically in pairs on each side of the jaw. At *c*, Fig. 13, is one of the *parotid glands*, at *c'* a *submaxillary gland*, and at *c''* a *sublingual gland*. The saliva passes from these glands through ducts into the mouth and serves to moisten and predigest the food preparatory to swallowing. The *tongue* mixes the saliva with the food and arranges the food in a suitable position for the action of the teeth.

The saliva contains a constituent, known as *ptyalin*, which changes the starch first into *dextrine* and then into sugar, the result being that the digestion of starchy food is begun in the mouth. Subsequently, the ptyalin is allowed to continue this digestion in the stomach, where the food may remain in one end for an hour or so without being acted on by the *gastric juice*, which is produced by the stomach.

30. The Stomach.—The chewed food passes through the *œsophagus d*, Fig. 13, into the stomach *e*, the junction between the *œsophagus* and the stomach being at *e'*. At *e''*, known as the *pylorus*, the contents of the stomach pass into the intestine. The end of the stomach adjoining the mouth *e'* serves mostly as a storehouse for food, so that enough food may be eaten to supply the body for several hours. The contents remain here at comparative rest, the walls of the stomach exerting only a general pressure, forcing the contents slowly toward the lower end, thus allowing the saliva time to complete its work.

The lower end of the stomach performs a series of wavelike, constrictive movements by means of the unstriated muscles in the stomach walls. These movements produce a thorough mixing of the food with the gastric



FIG. 15

juice, which exudes from the walls; simultaneously, the food is forced toward the pylorus.

31. As seen from the sectional view of the stomach, Fig. 15 (*a*), the inner membrane has a corrugated surface penetrated by ducts of numerous minute glands. An enlarged view of a portion of the membrane is shown at (*b*). The glands are known as *gastric glands* and serve to secrete the *gastric juice*

for digesting the food and for killing bacteria. A quantity of from $2\frac{1}{2}$ to 5 quarts of gastric juice is secreted in one day. The main constituent of this juice is water, to which is added a small percentage of *pepsin* and *rennin*, and about .2 per cent. of hydrochloric acid. Pepsin dissolves the connective tissue of animal foods, thus assisting in their subdivision; it also digests the proteids contained in the food.

As regards the digestion of proteids, it may be said that the function of the gastric juice is to split the compounds into others of less complex structures. The acid, besides assisting the pepsin in its action, serves to kill a great number of bacteria, thus reducing the number that may reach the intestines and cause trouble in the lower part of the alimentary canal.

When the contents of the stomach reach the pylorus, it is of a souplike consistency, and is then known as *chyme*.

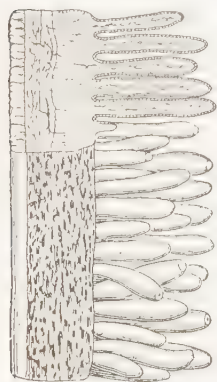


FIG. 16

32. Small Intestine.—Small quantities of chyme pass at intervals of a few minutes from the stomach through the pylorus *e''*, Fig. 13, into the upper portion of the small intestine *f*. This intestine constitutes the longest part of the alimentary canal, having a length of nearly 22 feet and a surface area of about 25 square feet.

The intestinal walls consist of two muscular layers, of which the inner one is built up of fibers arranged transversely, while in the outer one the fibers run lengthwise. The mucous membrane covering the inside of the intestine contains simple glands that discharge a digestive juice, and is also provided with minute finger-like projections, known as **villi**. These are about $\frac{1}{2}$ millimeter long and $\frac{1}{10}$ millimeter thick. The general arrangement of the villi may be seen from Fig. 16, which is a greatly enlarged section of a portion of the intestinal wall, showing some of the villi in cross-section. The villi perform the important function of absorbing the nourishment from the digested food and transmitting it to the blood.

33. The transverse, unstriated muscles of the small intestine perform a periodic contraction of the muscle walls in the manner illustrated in Fig. 17. Referring to the view at (a), it

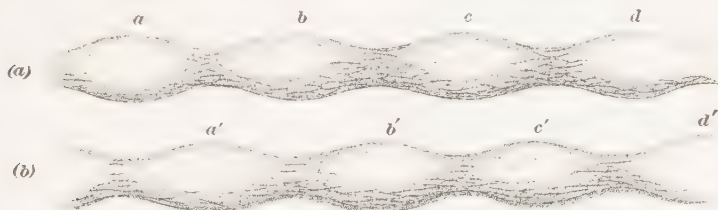


FIG. 17

is seen that certain portions of the wall are contracted while intermediate portions, as at *a*, *b*, *c*, and *d*, are not affected. Subsequently, the latter parts are contracted, as shown in the view at (b), while those previously contracted are allowed to expand to their original diameters, as at *a'*, *b'*, *c'*, and *d'*. It is easily seen that if these contractions are performed successively in a certain order, a wavelike motion is produced, which will propel the contents in the direction indicated by the arrows in Fig. 18.

34. Large Intestine.—At the lower right-hand side of the abdominal cavity the small intestine joins the **large intestine**, or **colon**, shown at *k*, Fig. 13. At the place of junction *l* is found the narrow sac *m*, known as the *appendix vermiformis*.



FIG. 18

The large intestine consists of three parts: (1) The *ascending* part on the right side; (2) the *transverse* part, passing from right to left at the level of the stomach; and (3) the *descending*

part on the left side, passing down to the *rectum n* with its opening *o*, the *anus*.

The large intestine has no villi, but has a great number of glands that discharge a juice which serves mainly to lubricate the walls of the intestine. As the chyme reaches the large intestine the useful portion of the food has, to a large extent, been absorbed, leaving behind connected tissues of vegetable and animal origin. This intestine is also provided with absorbing glands that continue the extraction of the nourishing portions of the chyme, and as this absorbing function exceeds that of the excretion glands, the result is that the chyme gradually loses its fluid portion and assumes a more solid consistency. The collected waste products pass eventually, as a solid mass, into the lower part of the descending portion of the colon and from there into the rectum; it is then known as *feces*.

35. Pancreas and Liver.—In the preceding description of the alimentary canal only the path followed by the food was considered, organs situated outside of this path, but acting on the food, being left out of consideration. The most important of these organs are the **pancreas** and the **liver**, shown in Fig. 13 at *g* and *h*, respectively. A duct *j* from the liver joins one from the pancreas, and the common duct connects with the small intestine at the place indicated in Fig. 13.

As the chyme leaves the stomach it is acid, so as to facilitate the action of the pepsin contained in the gastric juice. The alkaline juice delivered by the pancreas neutralizes the acid in the chyme and destroys the pepsin. The pancreatic juice contains the following three enzymes: (1) *Trypsin*; (2) *amyllopsin*; and (3) *steapsin*. The **trypsin** continues the action of the pepsin; **amyllopsin**, which is similar to saliva, converts the starches into sugar, while **steapsin** changes the fats into digestible fatty acids. The pancreatic juice performs a function of primary importance in intestinal digestion.

36. The fluid discharged by the liver is known as **bile**. The constituents of the bile do not all take active part in the digestive process, as some of them are waste products that use the intestines simply as a path of discharge. Other constituents

cooperate with the pancreatic juice in digesting fats, resulting in certain saponaceous combinations that are insoluble in the absence of bile.

The liver is constantly active in producing bile, which during digestion flows directly and more freely into the intestine. When the digestive process stops, the bile duct is closed and the bile produced by the liver flows into the *gall bladder* *i*, Fig. 13, where it is stored for future use.

37. Summary.—Food may be defined as a substance that, when taken into the body, will be oxidized or burned by it and thus furnish the necessary energy and means for maintaining the functions of the body. The foods, when taken into the system, are digested or split up by enzymes to make them dissolve and thus enable them to pass through the walls of the alimentary canal. Starchy foods are split into malt sugar by the ptyalin in the mouth and stomach, and by the amyllopsin in the intestine. The malt sugar and the ordinary sugar received by the mouth are split in the intestine into grape sugar, which is absorbed by the liver and used by the cells when they need it.

38. Within the cells the grape sugar is oxidized, water and carbon dioxide being delivered by the cells as waste products. In this manner the cells obtain their energy from the sugar.

The proteids contained in the food are split into peptones by pepsin in the stomach and by trypsin in the intestine. Fats are digested in the small intestine and, to some extent, also in the large intestine.

The digested portions of the foods are absorbed by the linings of the intestine and carried by the blood to the cells. The cells must have a constant supply of food, therefore there is stored in the body a certain amount of fat to act as a source of supply when food is lacking and in case of sickness.

Alcoholic drinks increase the secretion of various glands, but, on the whole, slacken the process of digestion. Alcohol also produces serious results by preventing the liver from changing the uric acid of the body into the harmless urea.



FIG. 19

CIRCULATORY SYSTEM

HEART AND BLOOD VESSELS

39. Elements of Circulatory System.—The term *circulation* is in this case applied to the circuit followed by the blood in passing from the heart through the body and back again to the heart. The blood is set in motion by the periodic contraction and expansion of the heart and passes from the heart through the paths provided for it throughout the body. The combination of the heart and the various blood vessels is known as the *circulatory system*. The distinctive purpose of this system is to carry the blood to all parts of the body. This blood, besides carrying food for the growth and proper action of all the organs of the body, also acts as a scavenger and carries away from the organs matter that would be harmful if allowed to remain. The blood vessels that carry the blood away from the heart are known as *arteries*; those that return the blood to the heart are known as *veins*; and the small vessels that connect arteries and veins are known as *capillaries*.

40. The pure blood, which is bright red in color, is carried

away from the heart by the arteries, which branch out all over the body like the branches of a tree, becoming gradually smaller and smaller, until they form a network of very fine tubes, the **capillaries**, which enter into the deepest parts of the different organs. Fig. 19 shows the arteries on the back of the hand and forearm. Subsequently, the capillaries reunite and form small **veins**; these combine gradually and form larger ones, which convey the blood back to the heart. When the blood reaches the veins, it is in an impure condition and dark in color, for while it passes through

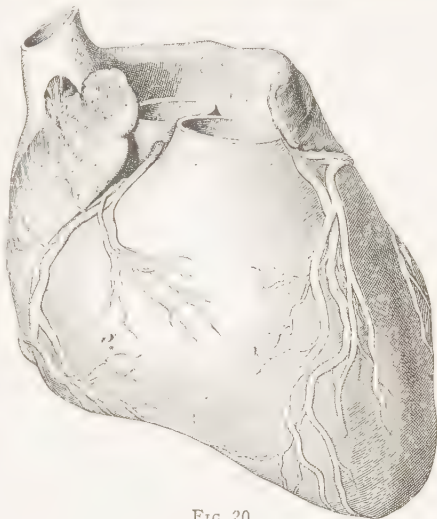


FIG. 20

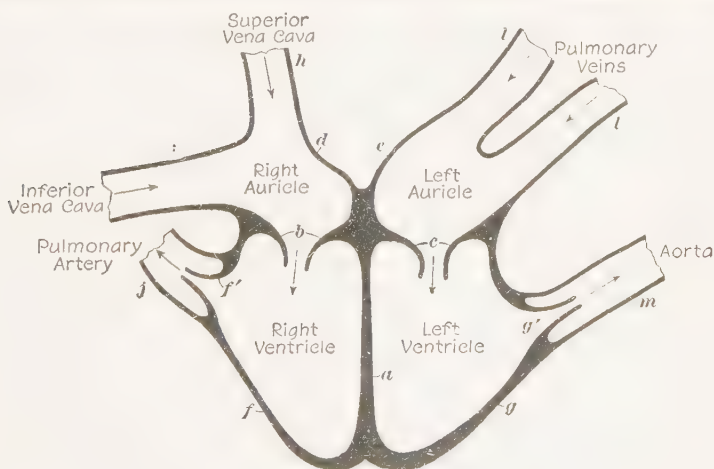


FIG. 21

the capillaries it gives up its oxygen and picks up any waste material that may be there.

41. The Heart.—From the diagrammatic view of the circulatory system, Fig. 24, and from the outside view of the heart, shown in Fig. 20, it is seen to be a hollow muscular organ of a conical shape. The heart lies just to the left of the center line of the sternum and near the latter, the large end being turned upwards and the point extending just below the left nipple, where it can be felt beating.

The diagrams in Figs. 21 and 22 give a general idea of the internal arrangement and operation of the heart, while Fig. 23 shows, diagrammatically, the entire circulation, similar reference letters representing similar parts in these diagrams. As the two sides of the heart act independently, they are, for rea-

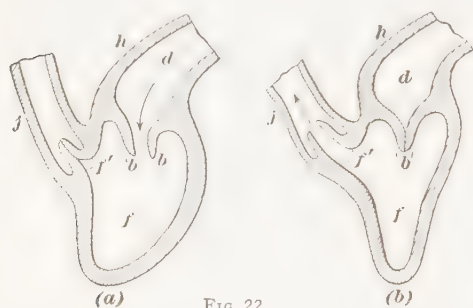


FIG. 22

sons of greater clearness, shown separate in Fig. 23, although, of course, there is but one heart.

42. Referring to Fig. 21, it is seen that there is a partition *a* extending from the base of the heart to its apex, thus dividing the interior into two chambers; these chambers are subdivided into two smaller ones by means of flaps, or *valves*, *b* and *c*. The upper chambers *d* and *e* are called *auricles*, and the lower ones *f* and *g*, the *ventricles*.

In the right auricle *d* there are two openings *h* and *i*, by which the impure blood enters. The upper one *h*, called the *superior vena cava*, receives the blood from the veins of the head and upper extremities, and the lower one *i*, called the *inferior vena cava*, receives the blood from the veins of the lower parts of the body. As soon as the right auricle *d* is full of blood, its walls contract and force the blood through the valve *b* into the right ventricle *f*. When this is full its walls contract and force the blood through the pulmonary artery *j* into the lungs *k*, Fig. 23, and from there into the left auricle *e*.

43. The actions of the valves in the right part of the heart may be seen more clearly in the diagrams, Fig. 22 (*a*) and (*b*), which show two views of the right auricle and ventricle. When the auricle *d* contracts, as shown in view (*a*), the valve flaps *b* open and allows the blood to enter the ventricle *f*. The full ventricle contracts, as in view (*b*), and the pressure transmitted by the blood closes the valve *b* and opens the valve *f'*, allowing the blood to enter the pulmonary artery *j*. The left portion of the heart operates in a similar manner. It should be noted that while Fig. 23 shows the *aorta m* as passing only in a downward direction, it is supposed to include a branch supplying the head with blood.

44. Referring to Figs. 21, 23, and 24, the blood passes from the right ventricle through the pulmonary artery *j* to the lungs *k* and from them through the veins *l* into the left auricle *e*, through the valve *c* and into the left ventricle *g*. This ventricle forces the blood into the large artery *m*, called the *aorta*, which begins at the back of the left ventricle, and into the carotid arteries *m'* to the head. The blood passes through this

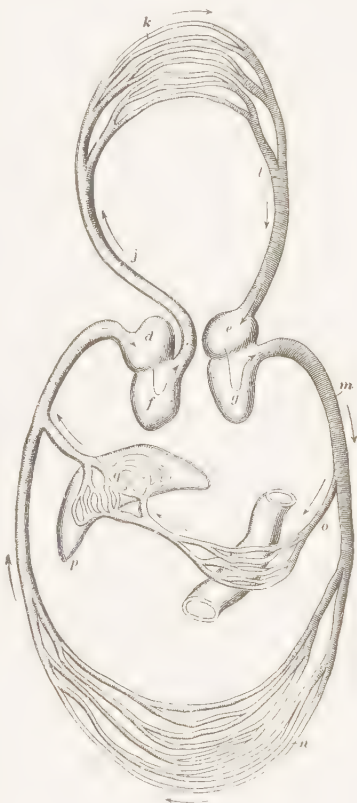


FIG. 23

aorta and the carotid arteries into the smaller arteries, which convey it through the whole body. The left ventricle has the thickest and strongest walls of any of the chambers of the heart, as it has to drive the blood through the whole body, excepting the lungs.

45. Both auricles act together, and then the ventricles, thus causing the double sound that is heard over the region of the heart. The pulsation that is felt in the arteries is caused by the action of the left ventricle driving a fresh supply of blood behind that which is already in the aorta. These pulsations are

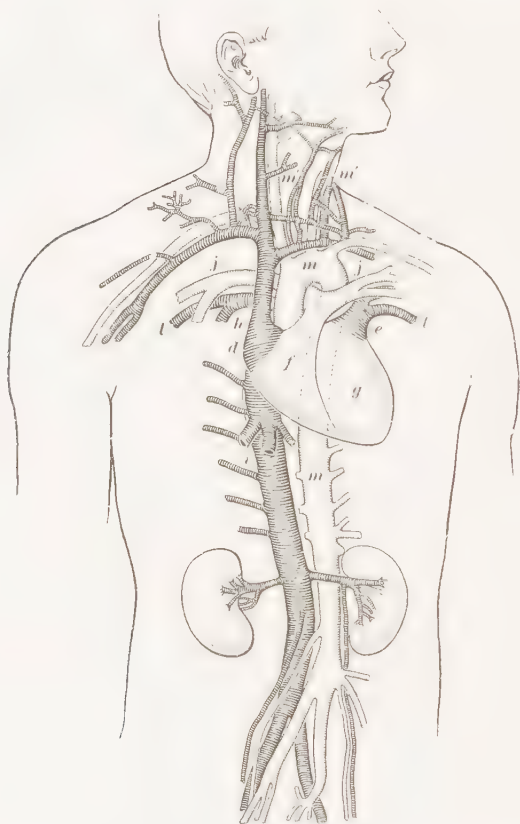


FIG. 24

felt only in the arteries, as the periodic variations of pressure disappear while the blood is passing through the capillaries; hence, when it reaches the veins, it flows in a steady stream. In Fig. 23, *n* represents the capillaries, greatly enlarged, found throughout the body, as in the brain, muscles, skin, kidneys, etc.

At *o* are shown the capillaries passing through the intestines, and at *q* those belonging to the liver *p*.

46. The heart beats from 70 to 80 times a minute, beats faster in women than in men, and varies in different individuals. The pressure exerted by the blood on the walls of the arteries is of such a strength that, if a vertical glass tube is connected with an artery, the blood will rise in the tube to a height of about 5 feet. The weight of blood discharged by both ventricles at each beat is about 4.5 ounces and the amount of work performed by each beat is about 1.25 foot-pounds, or nearly 130,000 foot-pounds in 24 hours.

47. The Blood.—The entire mass of blood contained in the human body is equal to about one-twentieth of the body weight. It is composed of a liquid part, the *plasma*, and of red and white blood *corpuscles* that float in the plasma. The *red corpuscles* constitute about 50 per cent. of the entire mass of blood. There are about 5,000,000 red corpuscles and 10,000 *white corpuscles* in a cubic millimeter of blood. The surface area of all the red corpuscles is about 30,000 square feet.

48. The *plasma* contains 90 per cent. of water and 10 per cent. of solids, such as proteids, salts, etc. required by the cells. The function of the plasma is to carry foods and water and to form a liquid in which the corpuscles may travel to all parts of the body.

The *white corpuscles* are cells of irregular shape that play an important role in destroying disease germs that may be present in the blood. The *red corpuscles* are small circular disks, slightly concave on each side. The function of the red corpuscles is to carry oxygen from the lungs to the tissues and carbon dioxide from the latter to the lungs. While the blood is carrying oxygen it retains its red color, but when passing through the capillaries and exchanging carbon dioxide for oxygen the color is changed to a dark blue.

LYMPHATIC SYSTEM

49. Lymphatic Vessels.—The lymphatics, or lymphatic vessels, constitute a system of minute, delicate, transparent vessels that have their origin at the surface of the body or in the cells of the tissues throughout the body. They constitute a fine capillary network throughout the body generally, even in those parts in which there are no blood vessels, as in the cartilages of the joints and in the cornea of the eye.

In order to nourish the various parts of the body, the liquid portion of the blood is constantly forced through the walls of the blood capillaries into the spaces between the cells of the tissues of the body. This liquid portion of the blood that flows in the spaces between the cells of the tissues, together with a certain number of white corpuscles that pass out through the walls of the capillaries, is known as the **lymph**. The lymphatics not only supply nourishment to the various parts of the body, but they also return to the blood the various impurities that are eventually to be thrown off by the skin, kidneys, lungs, and bowels.

50. Motion of Lymph.—The lymph moves in one direction only, that is, toward the heart. In the case of the blood the onward movement is due to the propelling power of the heart. The lymphatic system has not a similar central organ or pump and the movement of the lymph toward the center of the body is due to various influences of the organs and tissues through which it passes. Among these influences may be mentioned the contraction and expansion of the muscles in the arms and legs, and of those surrounding the abdominal cavity. Of great importance also is the suction produced in the muscles and tissues by the respiratory movements.

RESPIRATION

RESPIRATORY ORGANS AND THEIR FUNCTION

51. Purpose of Respiration.—Respiration is a function by which oxygen is absorbed from the surrounding medium and carbon dioxide returned to it. This function, which is in reality an oxidation process, is performed in every cell of the human body. The action of breathing, which is generally understood as respiration, and the circulation of the blood, must be considered simply as means for supplying the oxygen to the cells and for removing the carbon dioxide. If this gas were allowed to remain in the blood, it would soon cause suffocation; but the blood, as it passes through the lungs, comes in contact with air, which removes the impurities. The respiration process, as performed by the lungs, is divided into two stages: (1) **Inspiration**, or drawing in the air, and (2) **expiration**, or breathing out the air.

52. The Lungs.—The lungs, Fig. 25, are two large bodies that, with the heart, fill the cavity of the thorax, or chest. They rest on an arched muscle called the **diaphragm**, which separates the thorax from the abdominal cavity. The **trachea**, or **windpipe**, *a* is a flexible pipe that runs down along the front of the neck from the root of the tongue to a point on the level of the top of the breast bone, where it divides into two branches, known as the **bronchial tubes**. Of these the one indicated by *c* runs to the right side of the body, and the other *b* to the left. The bronchial tubes divide and subdivide until they form very small tubes, which at their inner ends are enlarged, so as to form air cells. The lungs are made up of these cells, which are covered by a network of capillaries, formed by the branching of the pulmonary arteries.

53. Inspiration and Expiration.—The act of **inspiration** is performed by contracting muscles which draw the ribs upwards, thus increasing the horizontal depth of the thorax from the breast bone to the spine. Simultaneously, the dia-

phragm becomes straight instead of convex, thus increasing the vertical depth of the thorax. The expanding lungs compel an influx of air through the windpipe and into the air cells of the lungs.

The act of **expiration**, or exhaling of the air, is caused by the muscles relaxing, thus allowing the ribs, by reason of their

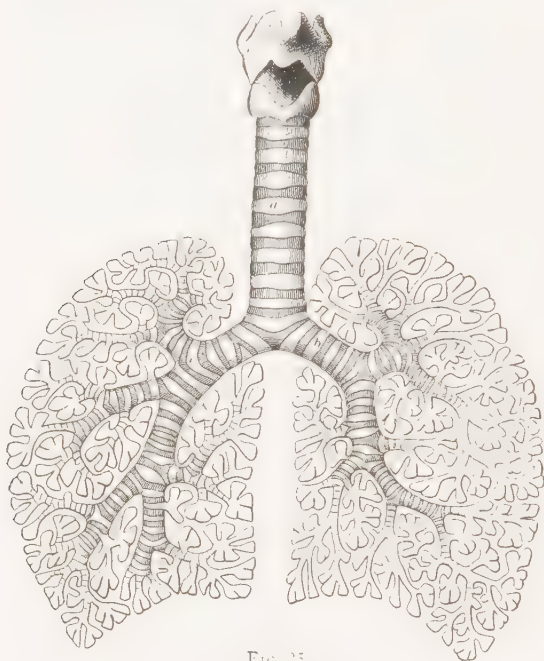


FIG. 23

elasticity, to resume their positions of rest, and the diaphragm to curve into a convex form. The capacity of the lungs being reduced, the air is forced out.

54. Effects of Respiratory Movements.—While the blood during the period of inspiration is passing through the capillaries that surround the air cells, it is brought into very close contact with the air contained in them. Under these circumstances the oxygen in the air is readily taken up by the blood in exchange for the carbon dioxide given up to the adjoining air cells, thus rendering the air in them impure.

At the succeeding expiration, this impure air is forced out of the lungs and is replaced by a supply of pure air at the next inspiration. To enable the respiration to be carried on properly, a sufficient supply of pure air is necessary, and this can be obtained, in the case of an enclosed space, only by proper ventilation.

EXCRETION

ORGANS OF EXCRETION

55. Body Waste Products.—In the various organs of the body waste products appear as the result of their activities. These products are produced by the process of oxidation in the lungs, arteries, and cells or by the digestive process in the intestines. An accumulation of these waste products would seriously interfere with the normal action of the various organs, hence the importance of their immediate removal. The term **excretion** is applied to the waste product itself, as well as to the process of removing it.

The principal organs of excretion are the lungs, the intestine, the liver, the kidneys, and the skin. Some of these organs perform the function of excretion in connection with other duties, as, for instance, the lungs and the intestine, as explained in preceding pages.

56. The Liver.—Below and near the diaphragm is found the largest gland in the body, the **liver**. It consists of a dark red substance divided by a fissure into two lobes, of which the right one is the larger. Its function as an excretive gland was explained in connection with the digestive process. Besides producing bile, the liver also produces a certain amount of urea, subsequently discharged in the urine. It has also the function of destroying poisonous substances produced in the intestines by the fermentation of food. When these poisons are taken up by the blood the latter is freed from them during its passage through the liver. The neutralized poisonous products are returned with the bile to the intestines. In case this function

of the liver is interrupted from any cause, the poisons pass into the arteries and produce results known under the general term *biliousness*.

57. The Kidneys.—The two bean-shaped organs, attached to the rear wall of the abdominal cavity below the diaphragm, are known as the **kidneys**. Their function is that of excreting the urea, uric acid, and water found in the blood. The gradual accumulation of waste matter in the kidneys finally finds its way into the *bladder*, from which organ the liquid waste matter leaves the body.

58. The Skin.—While the **skin** may and does serve as an organ of excretion, it is not one of its vital functions. It participates in the functions of the lungs and the kidneys in that it incidentally removes a small amount of carbon dioxide from the blood by diffusion, and by perspiration eliminates a certain amount of urea from the blood. But both of these functions can be performed entirely by the lungs and by the kidneys.

The main functions of the skin are: (1) To act as a protective covering for the underlying tissues; (2) to serve as an organ of feeling; and (3) to assist in maintaining a constant internal temperature of the body.

The outer layer of the skin is called the *epidermis*. The layer of connective tissue under the epidermis is the *dermis*; below the latter is found the *subcutaneous layer* in which fat is stored. The *nails* may be considered as modifications of the horny layer of the epidermis and serve as an important means for grasping objects.

SENSE ORGANS AND THE NERVOUS SYSTEM

SENSE ORGANS

59. Sensation in General.—Sensations may be caused by a special condition of an organ or of the body, as a whole. For example, changes of temperature may affect the whole body or a portion of it. Lack of food and water will affect some organs and not others. Sensations of pain may be pro-

duced in the whole body or in any part of it. The sensation caused by touch is general for any part of the skin. For these sensations no special organs exist.

60. Special Sense Organs.—Other sensations are produced in special organs constructed solely for this purpose, such as the eyes, the ears, the tongue with its nerves of taste, the nose with its nerves of smell. To these must be added the *sense of position*, presumably caused by the movement of the lymph in the inner ear. This sense of position serves as a means for establishing equilibrium of the body and for indicating changes in the position of the body through other means than the eyes.

61. Operation of Sense Organs.—The impulses that are received by the various sense organs are transmitted to the brain by nerves, where they produce sensations of light, sound, smell, taste, and touch. For example, when an object is *touched*, the epidermis is pressed down on the ends of the nerves of *touch*. In connection with the sense of touch it is interesting to note that there are distinct areas of the skin sensible to heat and others sensible to cold and that these are irregularly separated by areas sensible to touch.

62. Before a substance can be *tasted* it must be dissolved, so as to allow the molecules of the substance to descend among the taste cells and so affect them that impulses may be sent by the connecting nerve fibers to the brain.

Similarly, in the case of *smell* it is necessary that molecules should proceed from the smelling substance into the nasal chamber and come in contact with olfactory cells. Nerves connected with these cells transmit the received impulse to the brain and produce a corresponding sensation of smell.

63. *Sound* is transmitted by waves of air to the ear drum and from there to the inner ear where the auditory nerves are affected and convey their sensations to the brain.

The ear and the eye are sense organs of most intricate construction, and their actions are in some respects not quite understood. As regards the eye, it may be said that the lens

of the eye forms images on the *retina*, the inner coating of the rear chamber of the eye. In the retina are the fibers of the optic nerves which convey the impressions of the sight to the brain.

Considering the eye as a whole, it consists of a spheroid body protected by the eye socket, the eyelids, eyelashes, and eyebrows. It is constantly bathed in a fluid secreted by the *lachrymal glands*, the fluid being prevented from overflowing by the oily discharge of the *Meibomian glands*. The *iris*, which corresponds to the diaphragm of a photographic lens, gives the color to the eye. The central opening of the iris adjusts itself in accordance with the strength of the light, contracting in strong and expanding in weak light. The lens adjusts its curvature so that near as well as distant objects may be focused sharply on the retina.

THE NERVOUS SYSTEM

64. Function of Nervous System.—The function of the nervous system is to govern and coordinate the functions of the organs. For instance, during eating, a particular branch of the nervous system sets the digestive organs to work; another branch maintains the action of the heart and the lungs; other branches transmit the impressions of the sense organs to the brain. During walking, it is the nervous system that causes the right muscles to move at the correct moment, and so on through the numerous functions of the body.

65. Classification of Nervous System.—The nervous system is divided into two classes: (1) The *cerebro-spinal*, or *central*, system, and (2) the *sympathetic*, or *organic*, system. The **central nervous system** includes the brain and the spinal chord and controls the *voluntary muscles*, that is, those whose action is controlled by the will. The **sympathetic nervous system** controls the *involuntary muscles*, that is, those that are not subject to the action of the will. To this class belong the combinations of nerves that control the action of the stomach, the intestine, the heart, the blood vessels, etc.

66. Brain and Spinal Chord.—The brain is assumed to be divided into three principal divisions: (1) The *cerebrum*; (2) the *cerebellum*; and (3) the *medulla oblongata*, or *bulb*. Fig. 26 shows the brain, looked at from below, together with the spinal chord. The major portion of the brain is the cerebrum *a*, extending from front to back. At *b* is the cerebellum, at *c* the medulla oblongata, and at *d* the spinal chord, with its nerve branches, of which only a short portion of the main branches is shown.

In the interior of the cerebrum there is a cavity surrounded by corrugated walls, consisting of masses of gray matter, interspersed with masses of white matter representing bundles of nerve fibers. The outer surface of the cerebrum and the cerebellum is covered with gray matter, known as the *cortex*, which is connected with the highest functions of the brain. The spinal chord is a tubular structure of gray matter covered with a layer of white matter of fibrous nature, the whole protected by the vertebral column.

A general idea of the branches of nerves connected with the spinal chord may be obtained from the rear view of the human body shown in Fig. 27, in which the main nerve branches are indicated. Parts corresponding with those shown in Fig. 26 are indicated with similar letters. At *e* is shown the *great sciatic nerve*.

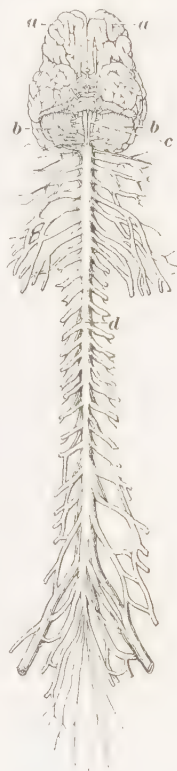


Fig. 26

67. Brain as Seat of Sensation.—The preceding examples of the action of sense organs show that in every case the impression received by a sense organ is transmitted to the brain. This is because the conscious sensation is developed in the brain and not in the sense organ. For example, if the auditory nerve is diseased or cut, so that the sound impression received by the nerves in the ear cannot be transmitted to the brain,

there is no sensation of sound. Similarly, if the optic nerve is cut there is no sensation of light. The ear and the eye may in both cases act in a perfectly normal manner, but being

unable to transmit their impressions to the brain, the latter, and therefore also its possessor, is unconscious of their presence.



FIG. 27

68. Function of the Spinal Chord.

It is a generally accepted theory that the spinal chord is the seat of the greater number of reflex actions performed in the trunk and by the limbs. By a *reflex action* is meant the involuntary action of a muscle. For example, if a hot iron is held near a hand, the latter is quickly withdrawn, the action being entirely automatic. In this case the sensation of heat is conveyed by nerves to the spinal chord where the impulse is transmitted to other nerves that operate muscles involved in moving the hand. As

other instances may be mentioned the heart, the stomach, the intestines, etc., which are all operated by reflex actions entirely outside the control of the will.

Experiments prove conclusively that reflex actions caused by outside stimuli have their seat in the spinal chord, which also acts as a path for nerve impulses to the brain. Thus, if a finger is pricked with a pin, it will instantly withdraw, and this action may be so quick, that the brain will not be conscious of pain until after the finger has moved.

POSOLOGY AND TOXICOLOGY

POSOLOGY

PRESCRIPTIONS AND THEIR ELEMENTS

INTRODUCTION

1. Definition.—Posology is that branch of medical science that deals with the doses of medicine.

2. Varieties of Doses.—The doses given in the United States Pharmacopœia and the National Formulary are the *average* doses for adults.

If the average is taken between the smallest amount of any medicine capable of producing the particular effect of a given drug and the largest amount necessary to produce the desired effect, that average quantity is considered as the **average dose**.

The **minimum dose** is the smallest dose capable of producing a medicinal effect.

The **maximum dose** is the largest dose that can be given with safety.

A **lethal dose** is one which, when taken internally, will produce death.

CALCULATION OF DOSES

3. Calculating Doses for Children.—Using the average dose as a basis, it is possible by means of **Doctor Young's rule** to calculate the required dose for children of various ages. The rule is as follows:

Rule.—*Divide the age of the child, in years, by the age plus 12, and multiply the quotient by the average dose.*

Or, expressed as a formula:

$$C = \frac{A}{A+12} D$$

in which

C = dose for a child;

A = age of child, in years;

D = average dose.

EXAMPLE.—If an average dose is 20 grains, what will be the dose for a child 3 years old?

SOLUTION.—Applying the formula,

$$C = \frac{A}{A+12} D = \frac{3}{15} \times 20 = 4 \text{ gr. Ans.}$$

4. Calculating Doses in Liquid Preparations.—The National Formulary gives the following rule for calculating the dose of each ingredient present in a teaspoonful, or fluid dram, of a preparation calling for 1,000 milliliters.

Rule.—*In formulas calling for 1,000 milliliters of product, multiply the quantity of substance in grammes by $\frac{8}{7}$ and divide by 20. The result is the quantity expressed in grains per fluid dram.*

EXAMPLE.—The formula for elixir pyrophosphate with quinine and strychnine calls for 1,000 milliliters of product and contains three active medicinal agents. The formula gives the following quantities of each substance:

Ferric pyrophosphate	35.00 Gm.
Quinine sulphate	8.75 Gm.
Strychnine	0.14 Gm.

It is required to find the dose of each of these substances per fluid dram.

SOLUTION.—Applying the formula for each of the substances contained in the formula the results are as follows:

The required quantity of ferric pyrophosphate is $\frac{35 \times \frac{8}{7}}{20} = 2 \text{ gr.}$; of quinine sulphate, $\frac{8.75 \times \frac{8}{7}}{20} = \frac{1}{2} \text{ gr.}$; of strychnine, $\frac{0.14 \times \frac{8}{7}}{20} = .008 = \frac{1}{125} \text{ gr.}$

Hence, the formula for 1 fluid dram, or 1 teaspoonful, of the preparation is as follows:

Ferric pyrophosphate	2 gr.
Quinine sulphate	$\frac{1}{2}$ gr.
Strychnine	$\frac{1}{125}$ gr.

Ans.

APPROXIMATE MEASURES AND EQUIVALENTS

5. Approximate Measures.—The following table gives the approximate values of various domestic measures in fluid drams and fluid ounces. However, these approximate doses should be avoided in filling prescriptions, as spoons, glasses, etc. vary greatly in capacity.

1 teaspoonful	=1 fluid dram	= 4 cubic centimeters=	4 mils.
1 dessertspoonful	=2 fluid drams	= 8 cubic centimeters=	8 mils.
1 tablespoonful	= $\frac{1}{2}$ fluid ounce	= 15 cubic centimeters=	15 mils.
1 wineglassful	=2 fluid ounces	= 60 cubic centimeters=	60 mils.
1 teacupful	=4 fluid ounces	=120 cubic centimeters=	120 mils.
1 tumblerful	=8 fluid ounces	=237 cubic centimeters=	237 mils.

6. Approximate Equivalents.—The equivalent values of grammes, mils, or cubic centimeters in grains or minims may be found in the following table :

TABLE I
APPROXIMATE EQUIVALENTS

Grammes, Mils, or Cubic Centi- meters	Grains or Minims	Grammes, Mils, or Cubic Centi- meters	Grains or Minims	Drams or Fluid Drams	Ounces or Fluid Ounces	Pounds, Awdp., or Pints
0.001	$\frac{1}{60}$	0.3	5			
0.003	$\frac{1}{20}$	0.5	8			
0.004	$\frac{1}{15}$	0.6	10			
0.008	$\frac{1}{8}$	0.8	12			
0.010	$\frac{1}{6}$	1.0	15			
0.015	$\frac{1}{4}$	4.0	60	I		
0.030	$\frac{1}{2}$	15.0		4		
0.050	$\frac{3}{4}$	30.0		8	I	
0.060	I	120.0			4	
0.100	I $\frac{1}{2}$	237.0			8	
0.200	3	475.0			16	I
0.250	4	950.0				2

DRUGS, CHEMICALS, AND PREPARATIONS USED IN PRESCRIPTIONS

7. Classifications.—In his prescriptions the physician makes use of drugs, chemicals, and various kinds of preparations. The latter may be prepared by chemical reactions or by various methods of manufacture, such as solutions, extracts, infusions, decoctions, mixtures, etc. The preparations may be classified in various ways, according to their physical condition, whether solid, liquid, etc.; or the classification may refer to their composition, depending on the substance employed in their preparation, such as water, alcohol, ether, etc.

8. Application of Table II.—In the following table the various substances are not classified according to any special system, but are arranged simply in alphabetical order for convenience in reference. Substances of similar nature are grouped together, such as acids, extracts, fluid extracts, syrups, etc. In these groups the distinctive terms are arranged alphabetically; if any of these terms are followed by an additional term, separated from the main term or terms by a comma, as *Acid, Lactic*, it is to be understood that the last term is to be read first. Hence, in this example the terms are to be read as *Lactic Acid*. In the case of *Lithium Citrate, Effervescent* the complete name is: *Effervescent Lithium Citrate*. Similarly, *Infusion of Senna, Compound* is to be read: *Compound Infusion of Senna*, and so on.

The name of each substance is followed by the dose in which it is usually administered. The doses are given in apothecaries weights and measures, the following abbreviations being used throughout : Ounce = oz.; dram = dr.; grain = gr.; fluid ounce = fl. oz.; fluid dram = fl. dr.; and minims = min.

The doses given in the table are *single* doses and not the sum of the doses to be given in one day. Also, the doses are not maximum, but average doses, and in the case of poisons, they are rather below the average. For instance, the average dose of phosphorus is $\frac{1}{10}$ grain; in the table the dose is only $\frac{1}{12}$ grain.

It is necessary for the student of pharmacy to be thoroughly familiar with the doses given in Table II.

TABLE II
DOSES OF IMPORTANT DRUGS, CHEMICALS, AND
PREPARATIONS

Name of Substance	Dose	Name of Substance	Dose
Acetanilide	4 gr.	Ammonium Valerate ...	7½ gr.
Acetphenetidin	7½ gr.	Amyl Nitrite	3 min.
Acid, Diluted Acetic	30 min.	Anise	7½ gr.
Acid, Benzoic	7½ gr.	Anise Water	15 min.
Acid, Carbolic	1 gr.	Anthemis	30 gr.
Acid, Camphoric	15 gr.	Antimony and Potassium	
Acid, Citric	7½ gr.	Tartrate	½ gr.
Acid, Gallic	15 gr.	Antidiphtheric Serum ..	500 units
Acid, Diluted Hydriodic ..	8 gr.	Antipyrine	4 gr.
Acid, Diluted Hydro-		Apocynum	15 gr.
bromic	1 fl. dr.	Apomorphine Hydro-	
Acid, Diluted Hydro-		chloride	⅒ gr.
chloric	15 min.	Arnica	15 gr.
Acid, Diluted Hydro-		Arsenic Trioxide	⅓ gr.
cyanic	1½ min.	Arsenous Iodide	⅒ gr.
Acid, Diluted Hypophos-		Asafetida	4 gr.
phorous	8 min.	Aspidium	60 gr.
Acid, Lactic	30 min.	Atropine	⅒ gr.
Acid, Diluted Nitric.....	30 min.	Atropine Sulphate	⅒ gr.
Acid, Nitrohydrochloric.	3 min.	Balsam of Peru.....	15 gr.
Acid, Phosphoric	30 min.	Balsam of Tolu.....	15 gr.
Acid, Salicylic	7½ gr.	Belladonna Leaves	1 gr.
Acid, Aromatic Sulphuric	15 min.	Belladonna Root	¾ gr.
Acid, Diluted Sulphuric.	30 min.	Benzaldehyde	½ min.
Acid, Sulphurous	30 min.	Benzoin	15 gr.
Acid, Tannic	7½ gr.	Benzosulphinide	3 gr.
Acid, Tartaric	7½ gr.	Berberis	30 gr.
Aconite	1 gr.	Betanaphthol	4 gr.
Aconitine	⅒ gr.	Bismuth and Ammonium	
Aloes	4 gr.	Citrate	2 gr.
Aloes, Purified	4 gr.	Bismuth Citrate	2 gr.
Aloin	1 gr.	Bismuth Subcarbonate ..	7½ gr.
Alum	7½ gr.	Bismuth Subgallate	4 gr.
Ammonia Water	15 min.	Bismuth Subnitrate	7½ gr.
Ammonium Benzoate ..	15 gr.	Bismuth Subsalcylate ..	4 gr.
Ammonium Bromide ...	15 gr.	Bitter Almond Water ..	1 fl. dr.
Ammonium Carbonate ..	4 gr.	Bromoform	3 min.
Ammonium Chloride ...	7½ gr.	Buchu	30 gr.
Ammonium Iodide	4 gr.	Caffeine	1 gr.

TABLE II—(Continued)

Name of Substance	Dose	Name of Substance	Dose
Caffeine, Citrated	2 gr.	Cinnamic Aldehyde	1 min.
Caffeine, Effervescent Citrated	60 gr.	Cinnamon, Ceylon	4 gr.
Calamus	15 gr.	Cinnamon, Saigon	4 gr.
Calcium Bromide	15 gr.	Cinnamon Water	4 fl. dr.
Calcium Carbonate, Precipitated	15 gr.	Cloves	4 gr.
Calcium Chloride	7½ gr.	Coca	30 gr.
Calcium Hypophosphate	7½ gr.	Cocaine	½ gr.
Calcium Phosphate, Precipitated	15 gr.	Cocaine Hydrochloride	½ gr.
Calendula	15 gr.	Codeine	½ gr.
Calumba	30 gr.	Codeine Phosphate	½ gr.
Camphor	2 gr.	Codeine Sulphate	½ gr.
Camphor Water	2 fl. dr.	Cod Liver Oil	4 fl. dr.
Camphor, Monobromated	2 gr.	Colchicine	1½ gr.
Cannabis, Indian	1 gr.	Colchicum Corm	3 gr.
Cantharides	1 gr.	Colchicum Seed	3 gr.
Capsicum	1 gr.	Colocynth	1 gr.
Caraway	15 gr.	Confection of Senna	60 gr.
Cardamon	15 gr.	Conium	3 gr.
Cascara Sagrada	15 gr.	Convallaria	7½ gr.
Cassia Fistula	60 gr.	Copaiba	15 min.
Castor Oil	4 fl. dr.	Copper Sulphate	4 gr.
Cerium Oxalate	1 gr.	Coriander	7½ gr.
Chalk Mixture	4 fl. dr.	Cotton Root Bark	30 gr.
Charcoal	15 gr.	Cotton Seed Oil	4 fl. dr.
Chalk, Prepared	15 gr.	Cresol	1 min.
Chimaphila	30 gr.	Creosote	3 min.
Chirata	15 gr.	Creosote Water	2 fl. dr.
Chloralformamide	15 gr.	Croton Oil	1 min.
Chloralformamide, Hydrated	15 gr.	Cubeb	15 gr.
Chloroform	5 min.	Cypripedium	15 gr.
Chloroform Water	4 fl. dr.	Dessicated Suprarenal Glands	4 gr.
Chondrus	4 dr.	Digitalis	1 gr.
Chrysarobin	½ gr.	Elaterin	1/10 gr.
Cinchine Sulphas	4 gr.	Elixir of Iron, Quinine and Strychnine Phosphates	1 fl. dr.
Cinchona	15 gr.	Emulsion of Almond	4 fl. dr.
Cinchona, Red	15 gr.	Emulsion of Asafetida	4 fl. dr.
Cinchonidine Sulphate	4 gr.	Emulsion of Chloroform	2 fl. dr.

TABLE II—(Continued)

Name of Substance	Dose	Name of Substance	Dose	
Emulsion of Cod Liver Oil	2 fl. dr.	Extract of Scopola.....	$\frac{1}{2}$ gr.	
Emulsion of Oil of Turpentine	1 fl. dr.	Extract of Stramonium	$\frac{1}{2}$ gr.	
Ergot	30 gr.	Extract of Taraxacum..	15 gr.	
Eriodictyon	15 gr.	Fennel	15 gr.	
Ether	15 min.	Fennel Water	4 fl. d.	
Ethyl Carbamate	15 gr.	Ferric Ammonium Sulphate	7 $\frac{1}{2}$ gr.	
Eucalyptol	5 min.	Ferric Chloride	1 gr.	
Eucalyptus	30 gr.	Ferric Citrate	4 gr.	
Eugenol	3 min.	Ferric Hydroxide with Magnesium Oxide	4 fl. oz.	
Euonymus	7 $\frac{1}{2}$ gr.	Ferric Hypophosphite ..	3 gr.	
Eupatorium	30 gr.	Ferric Phosphate (Soluble)	4 gr.	
Exsiccated Ferrous Sulphate	2 gr.	Ferric Pyrophosphate (Soluble)	4 gr.	
Extract of Aloes.....	2 gr.	Ferrous Carbonate, Saccharated	4 gr.	
Extract of Cascara Sagrada	4 gr.	Ferrous Sulphate	3 gr.	
Extract of Colchicum Corm	1 gr.	Fluid Extract of	Aconite	1 min.
Extract of Cimicifuga...	4 gr.		Apocynum	15 min.
Extract of Colocynth...	$\frac{1}{2}$ gr.		Belladonna Root	1 min.
Extract (Compound) of Colocynth	7 $\frac{1}{2}$ gr.		Berberis	30 min.
Extract of Digitalis....	$\frac{1}{2}$ gr.		Buchu	30 min.
Extract of Euonymus...	2 gr.		Calamus	15 min.
Extract of Ergot.....	4 gr.		Calumba	30 min.
Extract of Gentian.....	4 gr.		Capsicum	1 min.
Extract of Glycyrrhiza..	15 gr.		Cascara Sagrada ...	15 min.
Extract of Hematoxylon	15 gr.		Chimaphila	30 min.
Extract of Hyoseyamus	1 gr.		Chirata	15 min.
Extract of Indian Cannabis	$\frac{1}{2}$ gr.		Cinchona	15 min.
Extract of Krameria....	7 $\frac{1}{2}$ gr.		Coca	30 min.
Extract of Leptandra...	4 gr.		Colchicum Seed	3 min.
Extract of Malt.....	4 fl. dr.		Conium	3 min.
Extract of Nux Vomica	$\frac{1}{2}$ gr.		Convallaria	8 min.
Extract of Opium.....	$\frac{1}{2}$ gr.		Cubeb	15 min.
Extract of Physostigma	$\frac{1}{8}$ gr.		Cypripedium	15 min.
Extract of Quassia.....	1 gr.		Ergot	30 min.
Extract of Rhubarb....	4 gr.		Eriodictyon	15 min.
			Eucalyptus	30 min.
			Euonymus	8 min.

TABLE II—(Continued)

Name of Substance		Dose	Name of Substance		Dose
Fluid Extract of	Eupatorium	30 min.	Fluid Extract of	Stramonium	1 min.
	Frangula	15 min.		Sumbul	30 min.
	Gelsemium	1 min.		Taraxacum	2 fl. dr.
	Gentian	15 min.		Triticum	2 fl. dr.
	Geranium	15 min.		Uva Ursi	30 min.
	Ginger	15 min.		Valerian	30 min.
	Glycyrrhiza	30 min.		Veratrum	1½ min.
	Guarana	30 min.		Viburnum Opulus ..	30 min.
	Hamamelis Leaves ..	30 min.		Wild Cherry	30 min.
	Hydrastis	30 min.		Xanthoxylum	30 min.
	Hyoscyamus	3 min.	Frangula		15 gr.
	Ipecac	1 min.	Gambir		15 gr.
	Krameria	15 min.	Gamboge		2 gr.
	Lappa	30 min.	Gelsemium		1 gr.
	Leptandra	15 min.	Gentian		15 gr.
	Lobelia	8 min.	Geranium		15 gr.
	Lupulin	8 min.	Glycerin		1 fl. dr.
	Matico	1 fl. dr.	Glycerite of Hydrastis..		30 min.
	Pareira	30 min.	Glycerite of Phenol ..		5 min.
	Phytolacca	1½ min.	Glycerite of the Phos-		
	Pilocarpus	30 min.	phates of Iron, Qui-		
	Podophyllum	8 min.	nine, and Strychnine..		15 min.
	Pomegranate	30 min.	Glycerite of Tannic Acid		30 min.
	Quassia	8 min.	Glycyrrhiza		30 gr.
	Quercus	15 min.	Glycyrrhizin, Ammoni-		
	Quillaja	3 min.	ated		4 gr.
	Rhubarb	15 min.	Gold and Sodium Chlo-		
	Rose	30 min.	ride		1½ gr.
	Rubus	15 min.	Grindelia		30 gr.
	Sanguinaria	1½ min.	Guaiac		15 gr.
	Sarsaparilla	30 min.	Guaiacol		8 min.
	Sarsaparilla, Com-		Guaiacol Carbonate		15 gr.
	pound	30 min.	Guarana		30 gr.
	Savin	5 min.	Hamamelis Bark		30 gr.
	Scopola	1 min.	Hamamelis Water		2 fl. dr.
	Scutellaria	15 min.	Hedeoma		120 gr.
	Senega	15 min.	Hexamethylenamine		4 gr.
	Senna	30 min.	Homatropine Hydrobro-		
	Spigelia	1 fl. dr.	mide		128 gr.
	Squill	1½ min.	Honey		1 fl. dr.
	Stillingia	30 min.	Honey, Clarified		1 fl. dr.

TABLE II—(Continued)

Name of Substance	Dose	Name of Substance	Dose
Honey of Rose	1 fl. dr.	Lime Water	4 fl. dr.
Hops	30 gr.	Linseed Oil	1 fl. oz.
Hydrastine	$\frac{1}{2}$ gr.	Lithium Benzoate	15 gr.
Hydrastis	30 gr.	Lithium Bromide	15 gr.
Hydrastinine Hydrochloride	$\frac{1}{2}$ gr.	Lithium Carbonate	$7\frac{1}{2}$ gr.
Hyoscine Hydrobromide	$\frac{1}{128}$ gr.	Lithium Citrate	$7\frac{1}{2}$ gr.
Hyoscyamine Sulphate..	$\frac{1}{128}$ gr.	Lithium Citrate, Effervescent	120 gr.
Hyoscyamus	4 gr.	Lithium Salicylate	15 gr.
Infusion of Digitalis....	2 fl. dr.	Lobelia	$7\frac{1}{2}$ gr.
Infusion of Senna, Compound	4 fl. oz.	Lupulin	$7\frac{1}{2}$ gr.
Infusion of Wild Cherry	2 fl. oz.	Magnesium Carbonate ..	45 gr.
Iodine	$\frac{1}{10}$ gr.	Magnesium Oxide	30 gr.
Iodoform	4 gr.	Magnesium Oxide, Heavy	30 gr.
Iodol	4 gr.	Magnesium Sulphate ...	240 gr.
Ipecac	15 gr.	Magnesium Sulphate, Effervescent	240 gr.
Iron and Ammonium Citrate	4 gr.	Manganese Dioxide, Precipitated	4 gr.
Iron and Ammonium Tartrate	4 gr.	Manganese Hypophosphite	3 gr.
Iron and Potassium Tartrate	4 gr.	Manganese Sulphate	4 gr.
Iron and Quinine Citrate	4 gr.	Manna	240 gr.
Iron and Quinine Citrate, Soluble	4 gr.	Marrubium	30 gr.
Iron and Strychnine Citrate	2 gr.	Mass of Ferrous Carbonate	4 gr.
Iron Mixture, Compound	4 fl. dr.	Mass of Mercury	4 gr.
Iron, Reduced	1 gr.	Mastic	30 gr.
Jalap	15 gr.	Matico	60 gr.
Kino	$7\frac{1}{2}$ gr.	Matricaria	240 gr.
Koussou	240 gr.	Menthol	1 gr.
Krameria	15 gr.	Mercuric Chloride, Corrosive	$\frac{1}{20}$ gr.
Lactucarium	30 gr.	Mercuric Iodide, Red ...	$\frac{1}{20}$ gr.
Lead Acetate	1 gr.	Mercurous Chloride, Mild	1 gr.
Lemon Juice	1 fl. oz.	Mercurous Iodide, Yellow	$\frac{1}{2}$ gr.
Leptandra	15 gr.	Mercury with Chalk....	4 gr.
Lime, Chlorinated	4 gr.	Methyl Salicylate	15 min.
Lime, Sulphurated	1 gr.		

TABLE II—(Continued)

Name of Substance	Dose	Name of Substance	Dose
Methylthionine Hydrochloride	2 gr.	Oil of Juniper.....	3 min.
Mixture of Glycyrrhiza	7½ gr.	Oil of Lavender Flowers	3 min.
Mixture of Rhubarb and Soda	2 fl. dr.	Oil of Lemon.....	3 min.
Monohydrated Sodium Carbonate	4 gr.	Oil of Mustard, Volatile	½ min.
Morphine	½ gr.	Oil of Myristica.....	3 min.
Morphine Acetate	¼ gr.	Oil of Orange Peel.....	3 min.
Mucilage of Acacia.....	4 fl. dr.	Oil of Peppermint.....	3 min.
Mucilage of Elm.....	4 fl. dr.	Oil of Pimenta.....	3 min.
Mucilage of Sassafras Pith	4 fl. dr.	Oil of Rosemary.....	3 min.
Mucilage of Tragacanth	4 fl. dr.	Oil of Santal	8 min.
Musk	4 gr.	Oil of Sassafras.....	3 min.
Mustard, Black	120 gr.	Oil of Spearmint.....	3 min.
Mustard, White	120 gr.	Oil of Tar.....	3 min.
Myristica	7½ gr.	Oil of Thyme.....	3 min.
Myrrh	7½ gr.	Oil of Turpentine, Rectified	15 min.
Naphthalene	2 gr.	Oleoresin of Aspidium..	30 gr.
Nutgall	7½ gr.	Oleoresin of Capsicum..	½ gr.
Nux Vomica	1 gr.	Oleoresin of Cubeb.....	7½ gr.
Oil of Almond, Expresed	1 fl. oz.	Oleoresin of Ginger.....	½ gr.
Oil of Anise.....	3 min.	Oleoresin of Pepper.....	½ gr.
Oil of Betula.....	15 min.	Oleoresin of Lupulin....	3 gr.
Oil of Bitter Almond... ½ min.		Olive Oil	1 fl. oz.
Oil of Cajuput.....	8 min.	Opium	1½ gr.
Oil of Caraway.....	3 min.	Opium, Deodorized	1 gr.
Oil of Chenopodium....	3 min.	Opium, Granulated	1 gr.
Oil of Cinnamon.....	1 min.	Opium, Powdered	1 gr.
Oil of Cloves.....	3 min.	Orange Flower Water..	4 fl. dr.
Oil of Copaiba.....	8 min.	Orange Flower Water, Stronger	2 fl. dr.
Oil of Coriander.....	3 min.	Orange Peel, Bitter.....	15 gr.
Oil of Cubeb.....	8 min.	Orange Peel, Sweet.....	15 gr.
Oil of Erigeron.....	15 min.	Oxgall, Purified	7½ gr.
Oil of Eucalyptus.....	8 min.	Pancreatin	7½ gr.
Oil of Fennel.....	3 min.	Paraldehyde	30 min.
Oil of Gaultheria.....	15 min.	Pareira	30 min.
Oil of Hedeoma.....	3 min.	Pelletierine Tannate	4 gr.
		Pepo	1 oz.
		Pepper, Black	7½ gr.
		Peppermint Water	4 fl. dr.
		Pepsin	4 gr.

TABLE II—(Continued)

Name of Substance	Dose	Name of Substance	Dose
Phenol, Liquefied	1 min.	Potassium Dichromate..	$\frac{1}{4}$ gr.
Phenyl Salicylate	7 $\frac{1}{2}$ gr.	Potassium Hypophos- phite	7 $\frac{1}{2}$ gr.
Phosphorus	$\frac{1}{2}$ gr.	Potassium Iodide	7 $\frac{1}{2}$ gr.
Physostigma	1 $\frac{1}{2}$ gr.	Potassium Nitrate	7 $\frac{1}{2}$ gr.
Physostigmine Salicylate	$\frac{1}{16}$ gr.	Potassium Permanganate	1 gr.
Phytolacca	2 gr.	Potassium Sulphate	30 gr.
Pills, Compound Laxa- tive	2 pills	Potassium and Sodium Tartrate	120 gr.
Pills of Aloes	2 pills	Powder, Acetanilide, Compound	7 $\frac{1}{2}$ gr.
Pills of Aloes and Iron..	2 pills	Powder, Aromatic	15 gr.
Pills of Aloes and Mas- tic	2 pills	Powder, Compound Acetanilide	7 $\frac{1}{2}$ gr.
Pills of Aloes and Myrrh	2 pills	Powder, Compound Chalk	30 gr.
Pills of Asafetida.....	2 pills	Powder of Glycyrrhiza, Compound	60 gr.
Pills of Ferrous Carbon- ate	2 pills	Powder of Ipecac and Opium	7 $\frac{1}{2}$ gr.
Pills of Ferrous Iodide..	2 pills	Powder of Jalap and Quassia, Compound ..	7 $\frac{1}{2}$ gr.
Pills of Opium.....	1 pill	Powder of Rhubarb, Compound	30 gr.
Pills of Podophyllum, Belladonna, and Cap- sicum	1 pill	Pyrethrum	30 gr.
Pills of Phosphorus.....	1 pill	Quassia	7 $\frac{1}{2}$ gr.
Pills of Rhubarb, Com- pound	2 pills	Quillaja	4 gr.
Pilocarpine, Hydrochlo- ride	$\frac{1}{2}$ gr.	Quinine Bisulphate	4 gr.
Pilocarpine Nitrate	$\frac{1}{4}$ gr.	Quinine Hydrobromide..	4 gr.
Pilocarpus	30 gr.	Quinine Hydrochloride..	4 gr.
Pimenta	15 gr.	Quinine Salicylate	4 gr.
Piperine	3 gr.	Quinine Sulphate	4 gr.
Podophyllum	7 $\frac{1}{2}$ gr.	Resin of Jalap	2 gr.
Pomegranate	30 gr.	Resin of Podophyllum..	$\frac{1}{16}$ gr.
Potassium Acetate	30 gr.	Resin of Scammony....	3 gr.
Potassium Bicarbonate..	30 gr.	Resorcinol	2 gr.
Potassium Bitartrate ...	30 gr.	Rhubarb	15 gr.
Potassium Bromide	15 gr.	Rhus Glabra	15 gr.
Potassium Chlorate	4 gr.	Rose Water	4 fl. dr.
Potassium Citrate	15 gr.	Rose Water, Stronger ..	2 fl. dr.
Potassium Citrate, Ef- fervescent	60 gr.	Rosin	4 gr.
Potassium Cyanide	$\frac{1}{2}$ gr.		

TABLE II—(Continued)

Name of Substance	Dose	Name of Substance	Dose
Rubus	15 gr.	Sodium Phosphate, Ex-	
Sabal	15 gr.	siccated	15 gr.
Safrol	5 min.	Sodium Pyrophosphate..	30 gr.
Salicin	15 gr.	Sodium Sulphate	240 gr.
Salvia	30 gr.	Sodium Sulphite	15 gr.
Sanguinaria	2 gr.	Sodium Thiosulphate ...	15 gr.
Santonin	1 gr.	Solution, Antiseptic	1 fl. dr.
Sarsaparilla	30 gr.	Solution of Ammonium	
Sassafras	4 gr.	Acetate	4 fl. dr.
Savin	7½ gr.	Solution of Arsenous	
Scammony	4 gr.	Acid	3 min.
Scoparius	15 gr.	Solution of Arsenous and	
Scopola	¾ gr.	Mercuric Iodides	1½ min.
Scopolamine Hydrobro-		Solution of Chlorinated	
mide	1½ gr.	Soda	15 min.
Scutellaria	15 gr.	Solution of Chlorine,	
Senega	15 gr.	Compound	1 fl. dr.
Senna	60 gr.	Solution of Ferric Chlo-	
Serpentaria	15 gr.	ride	1½ min.
Serum, Antidiphtheric ..	500 units	Solution of Ferric Sub-	
Silver Nitrate	½ gr.	sulphate	3 min.
Silver Oxide	1 gr.	Solution of Hydrogen	
Sodium Acetate	15 gr.	Peroxide	1 fl. dr.
Sodium Arsenate	1/10 gr.	Solution of Iodine, Com-	
Sodium Arsenate, Ex-		pound	3 min.
siccated	2/10 gr.	Solution of Iron and	
Sodium Benzoate	15 gr.	Ammonium Acetate ..	4 fl. dr.
Sodium Borate	7½ gr.	Solution of Magnesium	
Sodium Bromide	15 gr.	Citrate	12 fl. oz.
Sodium Chlorate	4 gr.	Solution of Potassium	
Sodium Chloride	240 gr.	Arsenite	3 min.
Sodium Citrate	15 gr.	Solution of Potassium	
Sodium Hypophosphite..	15 gr.	Citrate	4 fl. oz.
Sodium Iodide	7½ gr.	Solution of Potassium	
Sodium Nitrate	15 gr.	Hydroxide	15 min.
Sodium Nitrite	1 gr.	Solution of Sodium	
Sodium Phenolsulphon-		Arsenate	3 min.
ate	4 gr.	Solution of Sodium Hy-	
Sodium Phosphate	30 gr.	droxide	15 min.
Sodium, Phosphate, Ef-		Solution of Sodium	
fervescent	120 gr.	Phosphate, Compound	2 fl. dr.

TABLE II—(Continued)

Name of Substance	Dose	Name of Substance	Dose
Sparteine Sulphate	$\frac{1}{2}$ gr.	Syrup of Ginger.....	4 fl. dr.
Spearmint	60 gr.	Syrup of Hydriodic Acid	1 fl. dr.
Spearmint Water	4 fl. dr.	Syrup of Hypophos-	
Spigelia	60 gr.	phites	2 fl. dr.
Spirit of Ammonia.....	15 min.	Syrup of Ipecac.....	4 fl. dr.
Spirit of Ammonia, Aro-		Syrup of Krameria.....	1 fl. dr.
matic	30 min.	Syrup of Lactucarium...	2 fl. dr.
Spirit of Anise	1 fl. dr.	Syrup of Lime.....	20 min.
Spirit of Bitter Almond	8 min.	Syrup of Rhubarb.....	2 fl. dr.
Spirit of Camphor.....	15 min.	Syrup of Rhubarb, Aro-	
Spirit of Ether	1 fl. dr.	matic	2 fl. dr.
Spirit of Glyceryl-Trini-		Syrup of the Phosphates	
trate	1 min.	of Iron, Quinine, and	
Spirit of Juniper, Com-		Strychnine	1 fl. dr.
pound	2 fl. dr.	Syrup of Rubus	1 fl. dr.
Spirit of Lavender.....	30 min.	Syrup of Sarsaparilla,	
Spirit of Nitrous Ether...	30 min.	Compound	4 fl. dr.
Spirit of Peppermint....	30 min.	Syrup of Senega.....	1 fl. dr.
Spirit of Spearmint....	30 min.	Syrup of Senna.....	1 fl. dr.
Staphisagria	1 gr.	Syrup of Tar.....	1 fl. dr.
Stillingia	30 gr.	Syrup of Tolu.....	4 fl. dr.
Storax	15 gr.	Syrup of Wild Cherry..	1 fl. dr.
Stramonium	1 gr.	Tamarind	240 gr.
Strontium Bromide	15 gr.	Tar	7 $\frac{1}{2}$ gr.
Strontium Iodide	7 $\frac{1}{2}$ gr.	Taraxacum	120 gr.
Strontium Salicylate ...	15 gr.	Terebene	8 min.
Strophanthin	$\frac{1}{200}$ gr.	Terpin Hydrate	2 gr.
Strophanthus	1 gr.	Thymol	2 gr.
Strychnine	$\frac{1}{4}$ gr.	Tincture of Aconite....	10 min.
Strychnine Nitrate	$\frac{1}{4}$ gr.	Tincture of Aloes.....	30 min.
Strychnine Sulphate	$\frac{1}{4}$ gr.	Tincture of Arnica....	15 min.
Sulphate of Iron, Gran-		Tincture of Asafetida..	15 min.
ulated	3 gr.	Tincture of Belladonna	
Sulphonmethane	15 gr.	Leaves	8 min.
Sulphonethylmethane ...	15 gr.	Tincture of Benzoin....	15 min.
Sulphur Iodide	30 gr.	Tincture of Benzoin,	
Sulphur, Precipitated ...	60 gr.	Compound	30 min.
Sulphur, Sublimed	60 gr.	Tincture of Cantharides	5 min.
Sulphur, Washed	60 gr.	Tincture of Capsicum...	8 min.
Syrup of Almond.....	1 fl. dr.	Tincture of Cimicifuga..	1 fl. dr.
Syrup of Ferrous Iodide	15 min.	Tincture of Cinchona...	1 fl. dr.

TABLE II—(Continued)

Name of Substance	Dose	Name of Substance	Dose
Tincture of Cinchona,		Tincture of Opium.....	8 min.
Compound	1 fl. dr.	Tincture of Opium, Cam-	
Tincture of Colchicum		phorated	2 fl. dr.
Seed	30 min.	Tincture of Opium, De-	
Tincture of Digitalis....	15 min.	odorized	8 min.
Tincture of Gambir,		Tincture of Bitter	
Compound	4 fl. dr.	Orange Peel	1 fl. dr.
Tincture of Gelsemium..	8 min.	Tincture of Sweet	
Tincture of Gentian.....	1 fl. dr.	Orange Peel	1 fl. dr.
Tincture of Ginger.....	30 min.	Tincture of Physostigma	15 min.
Tincture of Guaiac.....	1 fl. dr.	Tincture of Quassia....	30 min.
Tincture of Guaiac, Am-		Tincture of Rhubarb....	1 fl. oz.
moniated	30 min.	Tincture of Rhubarb,	
Tincture of Hydrastis...	1 fl. dr.	Aromatic	30 min.
Tincture of Hyoscyamus	15 min.	Tincture of Sanguinaria	15 min.
Tincture of Ipecac and		Tincture of Serpentaria	15 min.
Opium	8 min.	Tincture of Squill.....	15 min.
Tincture of Kino.....	1 fl. dr.	Tincture of Stramonium	8 min.
Tincture of Krameria...	1 fl. dr.	Tincture of Strophanthus	8 min.
Tincture of Lactucarium	30 min.	Tincture of Tolu.....	30 min.
Tincture of Lavender,		Tincture of Valerian....	1 fl. dr.
Compound	30 min.	Tincture of Valerian,	
Tincture of Lobelia.....	1 fl. dr.	Ammoniated	30 min.
Tincture of Musk.....	1 fl. dr.	Tincture of Veratrum...	15 min.
Tincture of Myrrh.....	15 min.	Triticum	120 gr.
Tincture of Myrrh and		Trituration of Elaterin..	$\frac{1}{2}$ gr.
Aloes	30 min.	White Oak	15 gr.
Tincture of Nutgall.....	1 fl. dr.	Wild Cherry	30 gr.
Tincture of Nux Vomica	10 min.		

LATIN TERMS USED IN PRESCRIPTIONS

9. **Latin Declensions.**—While it is not necessary that a pharmacist should be thoroughly conversant with Latin, still it is absolutely necessary that he should know the English equivalents of all the Latin terms employed in prescriptions. The following is a list of the terms in general use, together with their abbreviations and translations into English.

It is to be noted that some of the adjectives are followed by several letters separated by commas. For example, *albus, a,*

um. In Latin the adjective must have an ending corresponding with the noun that it qualifies. In this example the word *albus* is the masculine form, *alba* the feminine, and *album* the neuter form. Thus, if the adjective is combined with the feminine noun *cera*, it must be written *cera alba*, which means *white wax*. The neuter noun *santalum* combined with the Latin adjective for *red* is written *santalum rubrum*, meaning *red saunders*.

LIST OF LATIN TERMS USED IN PRESCRIPTIONS

Term or Phrase	Abbreviation	English Equivalent
Ablutio		A washing
Absente febre	Abs. febr.	In the absence of fever
Accuratissime	Accuratiss.	Most carefully
Acerbus		Sour
Ad	Ad	To, up to
Ad conciliandum gustum		To suit the taste
Ad defectionem animi...	Ad def. animi...	To fainting
Adde, or addantur, addendus, addendo	Ad. or add.	Add, or let them be added, to be added, by adding
Ad duas vices.....	Ad 2 vic.	At twice taking
Ad gratam aciditatem...	Ad grat. acid. ...	To an agreeable sourness
Ad hibendus		To be administered
Ad libitum	Ad lib.	At pleasure
Ad move, admovetur, admoveantur	Admov.	Apply, let it be applied, let them be applied
Ad partes dolentes.....	Ad. part. dolent.	To the painful parts
Ad secundum vicem.....		To the second time
Adstante febre	Adst. febre	When the fever is on
Ad tertiam vicem.....		For three times
Adversum	Adv.	Against
Æqualis, is, e.....	Æq.	Equal
Ætas		Age, time of life
Aggrediente febre.....	Aggred. febre...	While the fever is coming on
Agitator or agitetur	Agit. or agitet. ..	Shake, or let it be shaken
Albus, a, um.....	Alb.	White
Alternis horis		Every other hour
Alter		The other

LIST OF TERMS USED IN PRESCRIPTIONS—(Continued)

Term or Phrase	Abbreviation	English Equivalent
Amplus		Large
Ana	a. or aa.....	Of each
Ante	Ant.	Before
Aqua	Aq.	Water
Aqua bulliens	Aq. bll.	Boiling water
Aqua fervens	Aq. ferv.	Hot water
Aqua phagedenica flava ..	Aq. phaged. fl. ..	Yellow wash
Aqua phagedenica nigra ..	Aq. phaged. nig.	Black wash
Aqua saturni	Aq. saturn.	Lead water
Aquila alba	Aquil. alb.	Calomel
Argilla	Argill.	Clay
Aromaticus, a, um.....	Arom.	Aromatic
Aut		Or
Bacillum	Bacill.	Bougie
Balneum	Baln.	A bath
Balneum arene	Baln. aren. or B. A.	Sand bath
Balneum maris	Baln. mar. or B. M.	Salt-water bath
Balneum vaporis	Baln. vap. or B. V.	Steam bath
Balsamum	Bals.	Balsam
Bene	Ben.	Well
Bibe	Bib.	Drink
Bis in die.....	B. or bis i. d. ...	Twice a day
Bolus	Bol.	A large pill
Bonus		Good
Brevis, is, e.....	Brev.	Short
Bulliat, bulliant	Bull.	Let it, or them, boil
Cæruleus, a, um.....	Cærul.	Blue
Capiat	Cap.	May be taken
Calefactus, a, um.....	Calef.	Warmed
Capsula	Caps.	Capsule
Capsulæ amylicæ	Caps. amyl.	Cachets
Capsulæ gelatinosæ	Caps. gelat.	Gelatine capsules
Carbasus	Carbas.	Lint
Celeriter	Celer.	Quickly
Charta	Chart.	Paper
Charta cerata	Ch. cer. or chart. cerat.	Waxed paper
Charta pergamentoria...	Chart. pergam...	Parchment paper

LIST OF TERMS USED IN PRESCRIPTIONS—(Continued)

Term or Phrase	Abbreviation	English Equivalent
Chartula	Chartul.	Small paper
Cibus	Cib.	Food
Cito dispendetur.....	Cito disp.	Let it be dispensed quickly
Clausus, a, um.....	Claus.	Closed, or enclosed
Cochlear	Cochl.	Spoonful
Cochlear magnum	Cochl. magn. ...	A large, or table, spoonful
Cochlear modicum	Cochl. mod.	A medium, or dessert, spoonful
Cochlear parvum	Cochl. parv. ...	A small, or tea, spoonful
Coctio	Coct.	Boiling
Cœna or cena	Cœn.	Supper
Cola or coletur.....	Col. colet.	Strain, or let it be strained
Colaturæ	Colatur.	To, or of, the strained liquor
Colatus	Colat.	Strained
Collunarium	Collun.	A nose wash
Collutorium	Collut.	A mouth wash
Collyrium	Collyr.	An eye wash
Compositus, a, um.....	Comp. or co.	Compound
Congius	Cong.	Gallon
Consperge	Consp.	Dust or sprinkle
Contra		Against
Contunde or contusus...	Contus.	Bruise or bruised
Coque	Coq.	To boil
Cortex	Cort.	The bark
Cujus libet	Cuj. lib.	Of whatever you please
Cum	C.	With
Da, dentur, or detur....	D. det.	Give it, or they may be given
Da or dentur tales doses	D. dent. t. d.	Give, or let there be given, such doses
Decanta	Dec.	Pour off
Decoctum	Dec. or decoct..	Decoction
De die in diem.....	De d. in d.	From day to day
Detur or dentur.....	Det., dent.	Let there be given
Diebus alternis	Dieb. alt.	Every other day
Digere or digeretur....	Dig.	Digest, or it may be digested
Dispensetur or dispen- sentur	Disp.	Let there be dispensed

LIST OF TERMS USED IN PRESCRIPTIONS—(Continued)

Term or Phrase	Abbreviation	English Equivalent
Divide, dividatur, or dividendus, a, um.....	Div. or divid.	Divide, or it may be divided; to be divided
Dolor		Pain
Dosis or doses.....	Dos. or D.	Dose or doses
Durante dolore		While the pain lasts
Ejusdem	EjUSD.	Of the same
Emplastrum epispaticum	Empl. epist.	Blistering plaster
Emplastrum lyttæ	Empl. lytt.	Blistering plaster
Emplastrum vesicans or vesicatorium	Empl. vesic.	Blistering plaster
Enema or enemata.....	En.	An enema, a clyster
Epistomium	Epist. or epistom.	A stopper
Epistomium elasticum ..	Epist. elast.	A rubber stopper
Epistomium vitreum	Epist. vitr.	Glass stopper
Et		And
Ex aqua	EX. aq.	From or with water
Ex modo præscripto....	Ex. m. p.	As directed
Ex qua formentur.....	Ex qua form.	From which there may be formed
Extende	Extend. or Ext.	Spread
Extende supra alutam...	Ext. sup. alut. ..	Spread upon leather
Extende supra corium...	Ext. sup. cor.	Spread upon leather
Fervens	Ferv.	Boiling
Fervidus, a, um.....	Ferv.	Boiling
Fac, fiat, or fiant.....	F. or Ft.	Make, let it be made, let them be made
Farina		Flour
Fiat lege artis.....	F. l. a.	Let there be made according to (by the law of) art
Fiat secundum artem....	F. s. a.	Let there be made according to art
Filtra	Filt.	Filter
Flavus, a, um.....	Flav.	Yellow
Fluidus, a, um.....	Flu.	Fluid
Frigida, a, um.....	Frig.	Cold
Fuscus, a, um.....		Brown
Gargarisma	Garg.	A gargle
Gradatim		By degrees or gradually
Gramma or grammata..	Gm.	Gramme or grammes
Granum or grana.....	Gr.	Grain or grains

LIST OF TERMS USED IN PRESCRIPTIONS—(Continued)

Term or Phrase	Abbreviation	English Equivalent
Gutta or guttæ.....	Gtt. or gutt.	Drop or drops
Guttatim	Guttat.	By drops
Haustus	Haust.	A draught
Hirudo		A leech
Hora	H.	An hour
Hora decubitus	H. D.	At the hour of going to bed
Hora somnis	H. S. or Hor. somm.	Just before going to sleep
Idem		The same
Infunde	Inf.	Pour in, infuse
Infusum	Infus.	An infusion
Injectio		An injection
Lac		Milk
Lege artis	L. a.	According to art
Levitor	Levit.	Lightly
Liquor	Liq.	A solution
Lotio		A lotion
Macera	Mac.	Macerate
Magnus, a, um.....	Mag.	Large
Massa	Mass.	Mass
Mica panis	Mic. pan.	Crumb of bread
Minimum	M. or min.	A minim
Miscē	M.	Mix
Misce bene	M. bene	Mix well
Misce caute	M. caute	Mix cautiously
Misce or miscantur....	M. or misc.	Mix or let them be mixed
Mistura	Mist.	Mixture
Mitte, mittatur, mittantur	Mit.	Send or let it be sent, let them be sent
Modicus, a, um.....	Mod.	Moderate (sized)
Modo præscripto	Mod. præsc.	In the manner prescribed
Mora		Delay
More dictu	More dict.	In the manner directed
Mortarium		A mortar
Niger, nigra, nigrum....	Nig.	Black
Non-repetatur	Non-rep.	It is not to be repeated
Nox, noctis		Night
Numero	No.	By or in number
Obduce or obducatur....	Obduc.	Cover or let it be covered
Obductus, a, um.....	Obduct.	Covered or coated
Octarius	O.	A pint

LIST OF TERMS USED IN PRESCRIPTIONS—(Continued)

Term or Phrase	Abbreviation	English Equivalent
Oleosus, a, um.....	Oleos.	Oily or made of oil
Oleum	Ol.	Oil
Olla	Oll.	Jar
Omni hora	Omn. Hor.	Every hour
Omni bihorio	Omn. bih.	Every two hours
Omni mane	Omn. man.	Every morning
Omni nocte	Omn. noct.	Every night
Optimus, a, um.....	Opt.	Best
Ovum		An egg
Para, paretur, or paratus	Par.	Prepare, let it be prepared, or prepared
Pars or partes.....	Part. or P.	Part or parts
Partes æquales	P. or part æq. ..	Equal parts
Parvus, a, um.....	Parv.	Small
Per		Through, by
Pilula, pilule	Pil. or pilul.	Pill or pills
Post cibum	P. c., p. cib., or post cib.	After food
Potus		Drink
Post prandium	P. or post prand.	After dinner
Prandium	Prand.	Dinner
Pro		For
Pro re nata.....	P. r. n.	As occasion arises; as needed; occasionally
Pulvis or pulveres.....	P. or pulv.	Powder or powders
Pulvis grossus	Pulv. gross.	Coarse powder
Pulvis subtilissimus	Pulv. subt.	Very smooth powder
Quantum libet or quantum placet, or quantum vis, or quantum volue- ris	Q. l. or q. p., or q. v.	As much as you please
Quantum satis, quantum sufficit, or quantum sufficiat	Q. s.	A sufficient quantity
Quaque	Q. or q.	Every
Quaque hora	Q. h.	Every hour
Quotidie		Daily
Recens	Rec.	Fresh
Recipe	R., recip.	Take thou
Redactus in pulverem...	Red. in pulv. ...	Let it be reduced to powder

LIST OF TERMS USED IN PRESCRIPTIONS—(Continued)

Term or Phrase	Abbreviation	English Equivalent
Repetatur, repetantur . . .	Rept.	Let it be repeated, let them be repeated
Ruber, rubra, rubrum . . .	Rub.	Red
Scatula	Scat.	Box
Scilicet		Namely
Secundum artem	S. a.	According to art
Secundum legem	S. l.	According to law
Semen or semina	Sem.	Seed
Samis	Ss.	A half
Si opus sit	Si op. sit.	If it is best or necessary
Signa or signature	Sig.	Mark (label), or let it be marked (labeled)
Simplex	Simp.	Simple
Simul		Together
Singulorum	Sing.	Of each
Solutio	Sol. or solut.	Solution
Solve or solvatur	S. or solv.	Dissolve, or let it be dissolved
Spiritus vini rectificatus	S. v. r.	Alcohol
Spiritus vini tenuis	S. v. t.	Diluted alcohol
Spissus, a, um	Spiss.	Hard
Statim	Stat.	Immediately
Stilus		Pencil, stick, or crayon
Sume or sumatur	Sum.	Take, or let there be taken
Supra		Above
Talis or tales	Tal.	Such
Ter in die	T. or ter i. d.	Three times a day
Tere	Ter.	Rub or triturate
Tinctura	Tinct.	Tincture
Tritura	Trit.	Triturate
Una		Together
Uncia		An ounce
Unctulus		Besmeared, anointed
Unguentum	Ungt.	Ointment
Ustus, a, um	Ust.	Burned
Ut dictum	Ut dict.	As directed
Vas vitreum		A glass vessel
Vel		Or
Vitreus, a, um, or vitrum	Vitr.	Of glass, or glass

LATIN CARDINAL NUMBERS AND THEIR ENGLISH EQUIVALENTS

Unus	one	Septemdecim	seventeen
Duo	two	Octodecim or duode-	
Tres	three	viginti	eighteen
Quatuor	four	Novemdecim or unde-	
Quinque	five	viginti	nineteen
Sex	six	Viginti	twenty
Septem	seven	Viginti unus or unus	
Octo	eight	et viginti	twenty-one
Novem	nine	Trigenta	thirty
Decem	ten	Quadraginta	forty
Undecim	eleven	Quinquaginta	fifty
Dodecim	twelve	Sexaginta	sixty
Tredecim	thirteen	Septuaginta	seventy
Quatuordecim	fourteen	Octoginta	eighty
Quindecim	fifteen	Nonaginta	ninety
Sexdecim	sixteen	Centum	one hundred

INCOMPATIBILITY

10. Definition.—In pharmacy the term **incompatibility** means that two or more substances are unfit or unsuited to be mixed or associated together. When a physician writes a prescription he expects, as a rule, that there shall be no interaction between the ingredients of a mixture, but that they shall reach the patient in an unchanged condition. A prescription is called **incompatible** when the ingredients are of such a nature that, if brought together, a new compound would result; or a precipitate would be produced; or an explosion; or that some of the ingredients would become worthless; or that liquefaction would take place between powdered ingredients.

11. Classification of Incompatibilities.—Incompatibilities are generally divided into the following three classes: (1) *Chemical incompatibility*, where the change is the result of a true chemical reaction. For example, if sodium salicylate is prescribed with diluted sulphuric acid, salicylic acid is precipitated and sodium sulphate enters into solution. (2) *Pharmaceutical incompatibility*, where the change is the result of a physical condition. For example, if the solvent is unsuitable,

as when *cannabis indica* is added to water, in which case the resin is thrown out of the solution. (3) *Therapeutical incompatibility*, where the drugs prescribed have antagonistic medicinal properties, as when the prescription specifies chloral and strychnine, or digitalis and aconite. This class of incompatibility does not come within the field of the pharmacist, and he cannot presume to make any suggestions to the physician, who is supposed to be the sole judge as to the suitability of the prescription. It is only under circumstances that a mistake is evident that he should take cognizance of the error and call attention to it. Then, again, two drugs may be antagonistic in one respect and cooperate in another and it may be for the latter effect that the physician prescribes them.

12. Rules Defining Incompatibility of Drugs.

The following rules define the principal cases of incompatibility:

(1) Mineral acids are incompatible with the alkalies, their carbonates, and with lead.

(2) Metallic salts are precipitated by alkalies and by tannic acid.

(3) The alkaloids are incompatible with tannic acid and with caustic alkalies.

(4) All drugs are incompatible with their antidotes and with their reagents.

13. Examples of Prescriptions With Incompatible Ingredients.—In the following are given a number of prescriptions that contain incompatible ingredients. In each case is given the reason for the incompatibility, and this is printed in Roman, while the prescription itself is set in *Italic*.

1. \mathcal{R} *Calomel*
Antipyrine
M. ft. Pulv.

Calomel forms a poisonous compound with antipyrine.

2. \mathcal{R} *Spt. Ætheris Nit.*
Potassium Acetate
Potassium Iodide
Aqua q. s. ad.

The sweet spirits of nitre will liberate the iodine of the potassium iodide.

3. \mathcal{R} *Menthol*
Chloral
Talcum

Menthol in the presence of chloral will liquefy. Camphor acts similarly.

4. \mathcal{R} *Tr. Ferri Chloridi*
Sodii Benzoatis
Syr. Tolu
Aq. Menthae Pip.

In this prescription ferric benzoate is formed at once.

5. \mathcal{R} *Ferri Chloridi*
Potassium Iodide
Syrup
Aqua ad.

Ferric salts are incompatible with iodides, the iodine being liberated. Iron salts with bromides act similarly; that is, they liberate bromine.

6. \mathcal{R} *Arsenii Trioxidum*gr. XII
Ferri Reductum.....gr. XXIV
Pulv. Glycyrrhiza q. s.
M. f. Pillulae No. XII

The dose of arsenic trioxide in each pill will here be 1 gr., which is poisonous, as the average dose of arsenic trioxide is $\frac{1}{30}$ grain.

7. \mathcal{R} *Hydrargyri Bichloridi*
Syr. Hypophosphite
Syr. Sarsaparilla Co.
Aqua Menthae Pip.

The hypophosphites are strong reducing agents and will reduce the bichloride of mercury first to calomel and then to pure mercury.

8. \mathcal{R} *Argenti Nitras*
Ext. Glycyrrhiza
Pulv. Althaeae
M. f. Pill.

Silver nitrate becomes decomposed in contact with organic substances and therefore the mass of pills cannot be made with licorice or althæa. An inorganic substance, as kaolin, should be used.

9. *R* *Cocaine Hydrochloride*
 Sodium Borate
 Aqua q. s. ad.

The sodium borate being an alkali, it will precipitate the alkaloid cocaine.

10. *R* *Potassium permanganate*
 Glycerine q. s. ad.

An explosion will take place because oxidizing substances should not be mixed with organic substances.

11. *R* *Potassium Chlorate*
 Acidi Tannici

Same result as in No. 10 and for the same reason.

12. *R* *Morphine sulphate*
 Cocaine Muriate
 Acidi Tannici
 Aqua Camphora
 Aqua Distillata q. s. ad.

The tannic acid will precipitate the alkaloids morphine and cocaine.

13. *R* *Ferri Chloridi*
 Elixir Simplex
 Aqua Gaultheria ad.

Upon mixing, a violet-blue color is produced owing to the fact that gaultheria, which is chemically methyl salicylate, will react with the iron forming iron salicylate.

14. *R* *Ferri Chloridi*
 Tr. Cinchona ad.

An inky mixture will be formed owing to the fact that cinchona contains tannic acid, which will react with the iron and form ink.

15. *R* *Ferri Chloridi*
 Spt. Ætheris Nitrosi
 Salol
 Aqua q. s. ad.

Salol is phenyl salicylate, which with iron forms salicylate of iron.

16. \mathcal{R} *Morphine Sulphate*
Aromatic Spt. of Ammonia
Aqua Menthae Pip.

The alkaline ammonia will precipitate the alkaloid morphine.

17. \mathcal{R} *Strychnine Sulp.*
Potassii Bromide
Syrup
Aqua q. s. ad.

The strychnine sulphate will be precipitated in the form of strychnine bromide.

18. \mathcal{R} *Quinine Sulphate*
Acidi Sulphurici Dil.
Potassium Iodide
Syrup
Aqua ad.

This is an example of a double incompatibility. The sulphuric acid is incompatible with potassium iodide and forms hydriodic acid, which in decomposing liberates iodine. The latter combines with quinine and forms quinine iodide.

19. \mathcal{R} *Aconite*
Digitalis
Sach. Lactis
M. f. Pulvis

This is an example of therapeutical incompatibility, as aconite tends to reduce the action of the heart while digitalis will tend to increase its action.

20. \mathcal{R} *Calomel*
Ammonium Carb.
Sach. Lactis
M. et ft. Pulv.

This forms a black chemical compound, mercurous oxide.

21. \mathcal{R} *Silver Nitrate*
Sodium Chloride
Aqua Distillata

The silver nitrate will react with the sodium chloride and form an insoluble silver chloride.

22. \mathcal{R} *Acidi Chromici*
Alcohol

An explosion will result.

23. \mathcal{R} *Potassium Permang.*
Hydrogen Peroxide

The peroxide decolorizes the solution and decomposes the potassium permanganate.

24. \mathcal{R} *Iodine*
Oil of turpentine
Alcohol

The iodine should not be added directly to the turpentine, as great heat will be developed, resulting in setting the mixture on fire or in exploding it. The iodine should be dissolved in the alcohol and the oil of turpentine added slowly.

25. \mathcal{R} *Sol. Magendie*
Sol. Fowleri aa. q. s. ad.

Magendie's solution is a solution of an alkaloid, viz., morphine, while Fowler's solution contains the alkali potassium bicarbonate. Consequently, the alkali will precipitate the alkaloid owing to the fact that alkalies and alkaloids are incompatible.

26. \mathcal{R} *Antipyrine*
Spt. Ætheris Nitrosi
Spt. Frumenti
Syr. Tolu

This prescription is incompatible because sweet spirits of nitre and antipyrine form a poisonous green compound.

27. \mathcal{R} *Tinctura Ferri Chloridi*
Acid Phosphorici dilute.....aa. Fl. dr. 1
Syrupi.....qs. ad. Fl. oz. 2
Mix.

If mixed as written, ferric phosphate will be precipitated. Sufficient diluted phosphoric acid should be used to dissolve the precipitate, and the quantity of syrup diminished accordingly.

28. \mathcal{R} *Acid carbolic.....Oz. ss.*
Aqua dest.....Fl. oz. ss.

By employing half an ounce of glycerine instead of water, precipitation is prevented and a clear solution is obtained.

29. \mathcal{R} *Colld. flexilis*
Tinct. Iodi
Aquæ ammoniæ.....aa. *Fl. dr. 2*
Mix.

As collodion is incompatible with aqueous liquids, the water of ammonia should be replaced by the spirit of ammonia, which is of the same ammonia strength.

30. \mathcal{R} *Tr. Ferri Chloridi*
Spt. Ætheris Nitrosi
Mucilago Acacia.....aa. *Fl. dr. 4*
Syrup.....qs. *ad. Fl. oz. 3*
Mix.

If the tincture and mucilage are mixed directly, the result will be a jelly-like precipitate; but if the mucilage is first diluted with the syrup, and the tincture and spirit mixed and gradually added, with shaking, a clear liquid is produced.

31. \mathcal{R} *Potassi chloratis*.....Gr. 8
Acidi hydrochloric.....M. 8
Glycerin.....Fl. dr. $1\frac{1}{2}$
Aqua.....ad. Fl. oz. 2
Mix.

Pour the acid on the chlorate and stopper the vial. When the vial is filled with chlorine gas, add the water and lastly the glycerine; otherwise an explosion will result.

TOXICOLOGY

POISONS AND THEIR ANTIDOTES

INTRODUCTION

14. Definitions.—The term **toxicology** is derived from the Greek terms *toxikon* and *logus*, meaning *poison* and *discourse*, respectively. In the modern sense the term toxicology may be defined as the science that treats of the nature of poisons, their effects on the human or animal organism, their detection, the antidotes, and the treatment of diseases due to poisons.

15. By the term **poison** is meant any substance that causes injury, disease, or death, when applied to, introduced into, or developed within a healthy human or animal body. Poisons may be introduced into the system by the skin, lungs, mouth, ear, nose, vagina, or rectum.

Substances cannot be sharply classified as *poisonous* and *non-poisonous*. A poison may be administered in doses that produce beneficial effects; and, on the other hand, substances that ordinarily are considered as harmless may, when taken in quantities, have deleterious effects.

Again, in some cases poisons taken in large doses act as their own antidotes. For instance, zinc sulphate will under such circumstances act as an antidote and cause the stomach to eject it.

16. First-Aid Work by Pharmacists.—The treatment of poison cases belongs, in reality, to the physician, but cases occur, at times, where quick action is of vital importance, or where a physician is not available. It is under such circumstances that the pharmacist, through his knowledge of

poisons, their symptoms and antidotes, can intelligently render first aid until the physician arrives.

17. Acute and Chronic Poisoning.—**Acute poisoning** is produced by taking one large dose of poison, or smaller doses at short intervals, in either case administering enough poison to produce a visible disturbance of the bodily functions, serious injury, or death within a short time.

Chronic poisoning, sometimes referred to as *chronic intoxication*, is a condition produced by taking small quantities of poison over an extended period of time. The results may not be visible, or only partly so, but the small doses have an accumulating effect on the system, and is known as a *cumulative poison*. Eventually, there is gradual deterioration of tissues or an accumulation of poison sufficient to produce a poisonous effect. Painters, plumbers, and dye workers are frequently affected by chronic poisoning.

As examples of chronic poisoning may be mentioned the following: (a) *Mercurialism*, produced by mercury; (b) *saturnism*, or *plumbism*, produced by lead; (c) *argyria*, chronic poisoning with silver salts; (d) *bromism*, produced by bromides; (e) *iodism*, produced by iodides; and (f) *cinchonism*, produced by cinchona or quinine.

SPECIAL AND GENERAL ANTIDOTES

18. Special Antidotes.—An **antidote** is a substance that renders the poison harmless by either neutralizing the poison itself or by counteracting the effects of the poison. An antidote employed to counteract the particular properties of any one poison is a **special antidote**.

Special antidotes may be classified as *chemical*, *physiological*, and *mechanical*.

19. A chemical antidote is one which combines chemically with the poison, producing either a harmless, soluble substance or an insoluble substance. For example, in case of sulphuric-acid poisoning, magnesium oxide is given as an antidote to produce the harmless magnesium sulphate.

20. A **physiological antidote** is one that does not enter into chemical reaction with the poison, but is intended to produce an effect on the system opposite to that of the poison. For example, in aconite poisoning the effect on the heart by the poison is that of a sedative. As there is no chemical antidote, it is necessary to give a stimulant, such as digitalis, to counteract the sedative effect.

21. A **mechanical antidote** neither reacts chemically on the poison nor counteracts the effects on the system. It simply removes the poison from the system or protects the internal tissues from further attack by the poison. To this class belong the *emetics*, *cathartics*, and *demulcents*, such as eggs, milk, cream, oils, and flour with water.

22. **General Antidotes.**—Some antidotes are used alone or in combination for any case of poisoning and are therefore known as **general antidotes**. Among these remedies are included mechanical antidotes, such as emetics, cathartics, and demulcents, and also the physiologic antidotes classified as stimulants.

23. **Emetics** are drugs used to produce vomiting. For example, zinc sulphate, 20 grains; copper sulphate, 15 grains; mustard, $1\frac{1}{2}$ ounces; apomorphine, $\frac{1}{16}$ grain, hypodermically; syrup of ipecac, 1 to 2 teaspoonfuls. Vomiting may also be produced by mechanical means; for instance, by pushing a finger into the throat.

24. **Cathartics** are drugs used to cause an evacuation of the bowels. For example, magnesium sulphate, $\frac{1}{2}$ ounce in water; castor oil, $\frac{1}{2}$ ounce; and croton oil, 1 minim.

Stimulants are drugs given to increase the functional activity of the heart. For example, strychnine, $\frac{1}{60}$ grain; brandy; and caffeine.

Demulcents are substances used internally to soothe irritated tissues. For this purpose are used eggs, milk, cream, oils, and other mucilaginous substances.

25. **Universal Antidote.**—A **universal antidote** is one that is a combination of several antidotes and used wher-

ever the identity of the poison is unknown. An example of this kind is *Jeannel's universal antidote*, consisting of a solution of ferric sulphate, $2\frac{1}{2}$ ounces; magnesia, 2 ounces; animal charcoal, 1 ounce; water, 20 ounces.

PRINCIPAL CLASSES OF POISONS

26. Classification of Poisons.—Poisons are divided into the following five classes: (1) *Corrosive poisons*; (2) *irritant poisons*; (3) *neurotic or true poisons*; (4) *septic poisons*; and (5) *gaseous poisons*.

27. Corrosive Poisons.—Those poisons that mainly exert a local action upon the tissue with which they come in contact are known as **corrosive poisons**. They generally destroy the tissues and by this means mingle directly with the blood. The most important poisons of this class are the concentrated mineral acids, such as nitric, hydrochloric, and sulphuric acids; also oxalic and acetic acids, the alkalies and their carbonates (potassium, sodium, and ammonium hydroxides and carbonates). Also, corrosive salts, such as silver nitrate and antimony chloride.

The symptoms of corrosive poisoning follow immediately after contact with the poison. If taken internally they produce a sensation of acid, alkaline, or metallic burning pain in the mouth, throat, gullet, and stomach. Vomiting is induced; this, however, does not relieve the distress. The pain soon extends over the entire abdomen, accompanied by symptoms of shock and collapse. In some cases there may be staining of the mouth.

28. Irritant Poisons.—**Irritant poisons** include the dilute mineral acids, concentrated organic acids, lime, zinc, copper, barium, and mercuric salts; all compounds of arsenic and antimony; phosphorus, iodine, bromine, etc. Many kinds of food may under certain conditions become irritant poisons, especially after having been canned and subsequently exposed to the air.

An irritant poison produces a burning pain in the stomach after an interval of some minutes to several hours after the poison was taken, differing in this respect from the action of a corrosive poison. The pain is accompanied by or followed by vomiting, faintness, and purging, the vomited matter being often tinged with blood. Death results from the irritation produced and the subsequent inflammation, which ends in the complete exhaustion of the patient.

29. Neurotic or True Poisons.—Neurotic poisons are sometimes subdivided into the following classes: (*a*) *Narcotics*, or those producing sleep, such as opium; (*b*) *anesthetics*, or those producing insensibility, as, for instance, chloroform; (*c*) *deliriants*, or those producing delirium, as hyoscyamus; (*d*) *convulsives*, or those producing spasms, as strychnine; (*e*) *inebriants*, or those producing intoxication, as alcohol; and (*f*) *depressants*, or those producing marked depression, such as nicotine. The neurotic poisons exercise their action through the nervous system and, therefore, only after absorption into the circulating blood. They rarely produce any local action.

30. Septic Poisons.—To the class of **septic poisons** belong those derived from the microbes in the air, soil, etc., through abrasions of the skin, open wounds, or by the fangs or stings of venomous animals or insects, such as blood poisoning, dog or cat bites, stings of bees, or snakes.

31. Gaseous Poisons.—To the class of **gaseous poisons** belong carbon monoxide (charcoal fumes), carbon dioxide (chokedamp), marsh gas (firedamp), formaldehyde, ammonia, sulphurous oxide, illuminating gas, sewer gas, noxious vapors and gases from manufacturing establishments, or any other fumes, gases, or vapors that may produce poisonous effects by their inhalation.

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CORROSIVE POISONS

32. Mineral Acids.—Among **mineral acids** are included sulphuric, hydrochloric, nitric, nitrohydrochloric, and phosphoric acids.

Symptoms.—Staining of the mouth or throat; immediate pain; vomiting of black or reddish matter; severe burning in the stomach.

Antidote.—The patient is given any of the following substances: Chalk, lime water, whitewash, magnesia (this is the best), plaster from the wall, strong solution of soap. This is followed by stimulants, demulcents, tincture of opium, or morphine to relieve the pain. Neither an emetic nor a stomach pump is to be used to remove the poison, as the tissues are too weakened and may be destroyed. No carbonates or bicarbonates must be used, as they set free carbon dioxide in the presence of the acid, and the gas may be produced in a quantity sufficient to rupture the stomach. Stimulants and external heat should be applied to counteract depression and possible collapse.

33. Organic Acids.—Oxalic, tartaric, and acetic acids are included among the **corrosive organic acids**.

Symptoms.—Burning pain, constriction of throat, vomiting, and cold extremities.

Antidote.—Same as for mineral acids, except in the case of oxalic acid, for which only lime water or chalk is to be used, as alkalies form soluble and poisonous salts with oxalic acid. Subsequently, mucilaginous drinks, stimulants are given; also tincture of opium or morphine to relieve pain.

34. Poisonous Antiseptics.—Among the substances used as antiseptics are carbolic acid, phenol, resorcin, and creosote, which are all poisonous.

Symptoms.—Pain in the stomach and white stains in the mouth, odor of carbolic acid, blackish urine, coma, contracted pupils and, finally, death by collapse.

Antidote.—Sodium carbonate in warm water is used as an emetic, or a stomach tube is used, unless the quantity taken was very large and in concentrated form, in which case there may be instant death from paralysis of the respiratory organs. Magnesium or sodium sulphate should be given as a chemical antidote, which forms a non-poisonous compound. This should be followed by dilute alcohol and then stimulants, and muc-

luginous drinks. Tincture of opium or morphine is given if necessary to relieve pain.

35. Alkalies.—The caustic alkalies, hydroxides, and carbonates of sodium, potassium, and ammonium are very similar in their toxic effects. The main difference is that the potassium salts have a more depressing effect on the heart.

Symptoms.—Acrid, burning taste in the mouth, throat, and stomach, hoarseness, vomiting of blood and mucus; skin cold and with clammy perspiration; rapid pulse, pain over the abdomen, and diarrhea.

Antidote.—No stomach pump to be used, and no emetic, as the tissues rapidly soften from the action of the alkali. Well-diluted organic acids are given, such as vinegar, lemon juice, tartaric or citric acids. Vegetable and animal oils may be used, as olive or linseed oils, butter, lard, cream, and milk; mucilaginous drinks may be freely given. In case of weak pulse, heart stimulants may be used and, if required, opiates to relieve pain.

IRRITANTS

36. Salts of Antimony, Tartar Emetic, Wine of Antimony, or Oxide of Antimony.—Among the salts of antimony, the tartar emetic is the most important by reason of its frequent use as an emetic. These salts are readily soluble, hence more easily absorbed and more difficult to remove from the stomach.

Symptoms.—Metallic taste, nausea, violent vomiting of green-bluish matter; burning pain in the stomach and bowels; cramps and cold perspiration.

Antidote.—Vomiting should be assisted by draughts of warm water or the stomach may be washed out. Then, a cup of tea or a solution of tannin should be given. Mucilaginous drinks should be freely given. The heart action should be sustained by proper stimulants. In case of persistent nausea or of pain, tincture of opium or morphine may be administered.

37. Potassium Bichromate.—Where this preparation is used in manufacture it affects the mucous membrane of the

nose, causing inflammation and ulceration. Taken internally it has in some cases caused death.

Symptoms.—Violent purging, painful vomiting of yellow matter, dilated pupils, great depression.

Antidote.—Free use of lime water or magnesia in milk.

38. Arsenic, White Arsenic, Arsenous Trioxide.

Arsenic is used in arts and manufacture in many forms, among the most common being "Paris green" and "rough on rats." When arsenic is introduced at any point in the system, it seems to seek the digestive organs and the symptoms appear in most cases at these places.

Symptoms.—The symptoms appear in acute cases within half an hour, but may be delayed two to three hours. They appear as faintness, nausea, bloody stools, severe vomiting, severe burning pain in the mouth and the stomach, intense thirst; cold sweats, though at times the skin may be dry and hot.

Antidote.—The stomach should be emptied with an emetic. Raw eggs beaten in milk should be given, followed by freshly precipitated ferric hydroxide with magnesia. Then, stimulants are given, and opiates to relieve the pain.

39. Salts of Aluminum and Alum.—Acetate and sulphate of aluminum sometimes cause poisoning, their action being similar to metallic salts in general. Alum, if taken in large doses, acts as an irritant poison, but tends to act as its own antidote by producing vomiting, hence fatal cases are rare.

Symptoms.—Nausea, vomiting, cold perspiration, rapid and weak pulse.

Antidote.—After washing out the stomach with a solution of borax, sodium bicarbonate or calcined magnesia is given as an antidote.

40. Soluble Lead and Barium Salts.—Acetate of lead (sugar of lead) sometimes causes poisoning. Soluble lead salts are formed in lead pipes in the presence of chlorides or nitrates in water. Barium salts are used in the arts and may cause accidental poisoning.

Symptoms.—Nausea, vomiting, diarrhea, and other symptoms common to irritant poisons. In the case of lead poisoning there are sometimes cramps in the calves, contraction of abdominal muscles, and muscular twitchings.

Antidote.—The stomach is washed out and some soluble sulphate is given, as magnesium or sodium, to form an insoluble barium or lead sulphate. In the case of lead poisoning the pain may be relieved by morphine or hot applications to feet and abdomen.

41. Soluble Copper Salts.—Metallic copper is acted on by fruit acids, salt, oils, and solutions of sulphates, nitrates, and carbonates, forming soluble salts of copper.

Symptoms.—The peculiar taste known as “coppery,” nausea, vomiting of blue or green matter, pains in the stomach, connected with diarrhea. Cold perspiration, burning thirst. Dark-brown stools containing blood.

Antidote.—Albumen, white of egg, or milk is given, followed by an emetic. The albumen forms an insoluble compound with the copper and is removed by the emetic.

42. Soluble Iron Salts.—Poisoning by medicine containing iron, as tincture of ferric chloride, has resulted from taking large doses.

Symptoms.—Severe pains in the stomach, connected with prolonged constipation or diarrhea, also stoppage of the urine.

Antidote.—Sodium bicarbonate followed by an emetic or stomach tube.

43. Soluble Mercury Salts.—In surgery mercury salts are used extensively, as bichloride, corrosive sublimate, etc. Poisoning by these salts is quite frequent, either through an error or intentionally.

Symptoms.—Severe burning sensation in throat and stomach, intense thirst and nausea, connected with vomiting. Diarrhea, weak and rapid pulse, cold perspiration. Labored respiration, cramps in the limbs, loss of consciousness.

Antidote.—Albumen, white of egg, or milk is given, followed by an emetic. The albumen forms with mercury an insoluble

albuminate which is removed by the emetic. An excess of albumen should be avoided, as mercury albuminate redissolves in an excess of albumen. The proper amount is the white of one egg for every four grains of the poison.

44. Soluble Zinc and Tin Salts.—Ordinary salt and organic acid act on cooking utensils coated with zinc. Chloride and sulphate of iron are the salts that generally cause poisoning. Chloride of tin is used in some dyes and has caused serious poisoning by being absorbed through the skin.

Symptoms.—The zinc chloride is more serious in its results than the zinc sulphate. In either case there is a burning sensation in the throat and the stomach with persistent vomiting and diarrhea. Weak and rapid pulse. In extreme cases there are convulsions. The tin salts produce less serious results.

Antidote.—In either case a solution of sodium carbonate is given, after which the stomach is washed out and vomiting assisted with an emetic.

45. Soluble Silver Salts.—Nitrate of silver is frequently used in the arts and medicine.

Antidote.—A solution of ordinary salt is used to produce an insoluble silver chloride. This is followed with an emetic.

46. Iodine.—Poisoning by iodine is mostly caused by swallowing the tincture.

Symptoms.—Abdominal pains, vomiting, suppressed urine, and delirium.

Antidote.—Boiled starch paste is given, made thin enough to be used as a drink, or flour is mixed with water. This is followed with an emetic.

47. Phosphorus.—The phosphorus used in poisoning is generally derived from matches. The *red*, or *amorphous*, *phosphorus* is not poisonous, but the *yellow* variety is violently poisonous and kills by depriving the blood of oxygen.

Symptoms.—Abdominal pains, severe vomiting, the matter having an odor of garlic, jaundice, suppressed urine, delirium. The vomited matter, which is luminous in the dark, is nearly

black and similar to coffee grounds. In general, the pulse is weak and quick, and there is at first a high temperature, gradually falling, until it becomes very low. Sometimes the nerves are greatly affected, and there are fainting spells combined with cramps in the limbs.

Antidote.—A 1-per-cent. solution of permanganate of potassium is used for washing out the stomach and to oxidize the poison. Copper sulphate is also recommended as an emetic and as a means for making the phosphorus insoluble. This is followed by a cathartic. Oils must not be given as they increase the solubility of the phosphorus and enable it to act more quickly. It is claimed that old or resinified oil of turpentine is an exception to this rule by reason of its solidifying effect on the phosphorus. Then, mucilaginous drinks are given, and opium, if necessary.

48. Cantharides, Colchicum, Gamboge, Colocynth, Elaterium, Croton Oil, and Oils of Pennyroyal, Savin, and Tansy.—These oils act as irritants and the symptoms produced are, in general, quite similar.

Antidote.—In any of these cases it is advisable to give albumen or white of egg in milk, followed by a little tannin and an emetic. In the case of cantharides no oils or fats should be given due to their solubility in oils.

49. Poisonous Meat, Fish, Lobsters, Ice Cream, Etc.—During the decay of food products, in particular canned foods, various substances are formed that in many respects are similar to vegetable alkaloids in their action. These products, which rapidly change during exposure to air, develop various kinds of compounds. Some of these are poisons and some are not; they are known under the term *ptomaines*.

Symptoms.—On the whole the physiologic action of these products is similar to the irritant poisons previously described. There is nausea and vomiting 3 to 4 hours after the food is taken; also great depression. At times there develops scarlet rash; young persons may suffer from convulsions. The pupils are either dilated or contracted. In general the patient recovers.

Antidote.—Vomiting should be encouraged by giving copious drafts of warm water; stimulants are given, and tincture of opium or morphine to relieve pain. A solution of tannin may be given; when vomiting ceases a dose of castor oil is advisable.

NEUROTICS

50. Narcotics: Opium, Morphine, Laudanum, and Paregoric.—The principal neurotic poisons, opium and morphine, are similar in their actions, though in some respects morphine is less active in deranging the digestive and urinating processes.

Symptoms.—Drowsiness, giddiness, stupor, insensibility, slow breathing, cool, clammy skin, and contracted pupils.

Antidote.—First, an emetic should be given. Then, to oxidize the morphine a 1-per-cent. solution of potassium permanganate is given, the harmless oxymorphine being the result. A strong decoction of coffee is now administered, followed by an emetic. Tannic acid is also advisable by reason of its precipitating effect on all alkaloids, rendering them insoluble. Atropine may be given hypodermically in $\frac{1}{100}$ -grain doses to encourage respiration. For the purpose of maintaining deep inspiration the patient should be kept awake by pinching, shouting in his ears, dashing hot and cold water on his face, walking, and other exercises.

51. Aconite.—Poisoning may be caused by eating the roots of monkshood or wolfsbane or by swallowing the medical preparation.

Symptoms.—Burning sensation on the tongue, general numbness, tingling sensation in the mouth and throat, giddiness, muscular depression, and delirium. Lowering of temperature, with clammy perspiration; oppressed breathing.

Antidote.—Avoid emetics. Make an effort to siphon contents of stomach. Tannic acid is used to precipitate the aconite and render it insoluble. This is followed by a liberal dose of castor oil. Stimulants are applied internally as well as externally. Artificial respiration may be performed by raising and lowering the arms or by giving inhalations of oxygen.

52. Hydrocyanic, or Prussic, Acid, Potassium Cyanide, Cherry-Laurel Water.—Hydrocyanic acid is one of the most deadly poisons and its action is so quick that antidotes can rarely be administered in time to save the patient.

Symptoms.—If a large dose is taken there is almost instant collapse. In case of a smaller dose there is difficulty in breathing, faintness, and nausea. There may be an odor of peach kernels.

Antidote.—Peroxide of hydrogen and potassium permanganate slowly neutralize the poison by oxidation. More quick in its action is a mixture of ferrous, or ferric, sulphates with carbonate of potassium, calcined magnesia being given to keep the contents of the stomach in an alkaline condition. External and internal stimulants and artificial respiration are required to maintain life until the poison is neutralized.

53. Alcohol, Cocculus Indicus, Nitrobenzene, Anilin.—The symptoms are not the same in cases of poisoning with these substances, but they may be counteracted in the same manner.

Antidote.—Emetics are given or the stomach pump is applied. Then, a weak solution of ammonium carbonate is given, followed by stimulation and artificial respiration.

54. Delirians: Belladonna, Stramonium, and Hyoscyamus.—The symptoms produced by eating any parts of these plants are very similar, and as the same antidotes are used, they may be considered under the one head of delirians.

Symptoms.—Intense thirst, flushed face, skin sometimes covered with rash, as in scarlet fever. Dilation of pupils, double vision; the patient appears vivacious and excited. In case of a large dose there is fall of temperature, feeble pulse, cold perspiration, stupor, and sometimes convulsions.

Antidote.—As tannic acid is an antidote for all alkaloids, a solution of it should be given to precipitate the alkaloid atropine present in belladonna, thus rendering it insoluble. This should be followed by an emetic, which in this case will be sluggish in its action; then, stimulants are given. It is of vital importance that artificial respiration is maintained, as by this

means the patient is more likely to recover, even in the case of a large dose.

55. Neurotics Producing Convulsions: Nux Vomica, Brucine, and Strychnine.—As strychnine is the active agent in nux vomica and brucine, they will be considered in common.

Symptoms.—Intensely bitter taste, followed in a few minutes by twitching of the muscles of the limbs. Subsequently the muscles are highly flexed, thus interfering with respiration. The head is drawn back and the body arched. Finally, convulsions. If the intervals between convulsions are short the patient will die from exhaustion.

Antidote.—First, an emetic is given; then a solution of tannin, followed by a cathartic. The patient must be kept warm and quiet, and to suppress the convulsions chloroform is administered by inhalation.

56. Depressants: Digitalis, Tobacco, Lobelia, Colchicum, and White Hellebore.—All of these poisons have one effect in common, that of muscular depression with a consequent cessation of action of the respiratory and cardiac muscles.

Symptoms.—Great depression, nausea, vomiting, irregular heart action.

Antidote.—Solution of tannin should be given as an emetic; in some cases this is dangerous by reason of the depressing effect. In its place the stomach should be washed out with the solution. The patient should be kept in a horizontal position. The depressive effects are counteracted by stimulants and external heat. Purgatives are also given.

SEPTIC POISONS

57. Snake Poison.—Poisoning may be caused by the bite of a poisonous snake, in which case it is well to note that this is rarely fatal.

Symptoms.—Swelling around the wound, increased pulse. Intense thirst. Gradually the pain increases, accompanied by

a discoloration of the affected part. Nausea and cold perspiration.

Antidote.—A handkerchief is tightly wound around the limb between the wound and the heart to confine the poison to a limited area. Then, the wound is washed thoroughly and painted with a 25-per-cent. solution of carbolic acid or tincture of iodine. The wound may be sucked without danger, as the poison is harmless unless introduced into the circulation, the main point being to remove as much of the poison as possible. The heart action is sustained by repeatedly giving small doses of strychnine. Whisky is also given, as it is known to destroy the poison if the latter should reach the stomach.

58. Rabies.—If bitten by a dog, the wound should be cauterized at once, for which purpose nitric acid should be used. Pasteur treatment should be administered at the earliest opportunity.

59. Poisoned Wounds and Stings.—The poisoned wound, as well as its surroundings, should be painted with a 25-per-cent. solution of carbolic acid. Stimulants should be given internally.

In case of stings by insects, the stinger should be extracted, if left behind. A paste made of baking soda and water may be applied; or the wound may be washed with weak ammonia water.

GASEOUS POISONS

60. Sulphuretted Hydrogen, Carbon Monoxide, Carbon Dioxide, Nitrous Fumes, Illuminating Gas, Sulphurous Oxide, Coal Gas, Marsh Gas.—The symptoms produced by any of these gases are similar in so far that they produce great muscular weakness, giddiness, and a strong tendency to sleep.

Antidote.—In all cases of gaseous poisoning the patient should be removed at once to fresh air. The clothing should be loosened to facilitate respiration, and artificial respiration administered. If possible, inhalation of oxygen should be given.

Stimulants should be administered. Alternate hot and cold douches on head and chest.

61. Ammonia Gas.—Treatment as in the preceding case. In addition to this the patient should be allowed to inhale chlorine gas, as developed by bleaching powders or chlorine water.

62. Chlorine Gas.—A bottle of strong ammonia is held to the nostrils. The chlorine gas combines with the ammonia gas and forms the harmless ammonium chloride.

63. Anesthetics: Vapors of Chloroform and Ether.—Artificial respiration must be performed persistently. Alternate hot and cold douche on head and chest. Stimulants must be by the rectum or hypodermically.

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